Ring-Collapsed Radical Alternating Copolymerization (RCRAC) of Homocyclic Compounds ob Group 15 Elements with Acetylenic Compounds(Dissertation_全文)

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Preface

The studies presented in this thesis have been carried out under the direction of Professor Yoshiki Chujo at Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University during April, 1998 - March, 2004. The studies are concerned with ring-collapsed radical alternating copolymerization (*RCRAC*) of homocyclic compounds of Group 15 elements with acetylenic compounds.

The author wishes to express his sincerest gratitude to Professor Yoshiki Chujo for his kind guidance, valuable suggestions, and warm encouragement throughout this work. The author is deeply and heartily grateful to Associate Professor Kensuke Naka for his constant advices and helpful discussions during the course of this work. The author is also indebted to Dr. Yasuhiro Morisaki for his valuable suggestions and discussions. The author would like to thank Ms. Akiko Nakahashi and Ms. Mia D. Bravo for their great contribution to this work and is thankful to all the members of Professor Chujo's group for their active collaborations.

The author wishes to express his special thanks to Professor Ian Manners at Department of Chemistry, University of Toronto for his kind support and valuable suggestions in the author's stay in Canada.

Finally, the author expresses his deep appreciation to his friends and family, especially his parents, Yuji and Chizuyo, for their continuous assistance and encouragement.

Tomokazu Umeyama

March 2004

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General Introduction

Organic and Inorganic Polymers

Organic Polymers

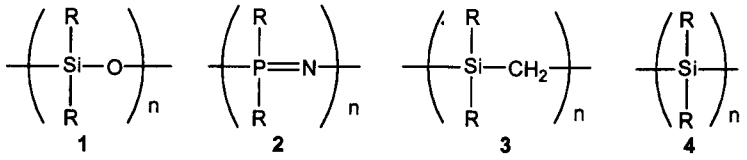
Despite the fact that carbon is not a particularly abundant element, the overwhelming majority of synthetic macromolecules known today are characterized by a backbone that contains either only carbon or carbon in combination with oxygen, nitrogen, or sulfur. The development in science of such "organic polymers" can mainly be attributed to the sophisticated state of organic synthesis as well as the exploitation of cheap and convenient fossil carbon sources. Molecules with multiple bonds capable of participating in addition polymerization and difunctional groups that act as monomers for polycondensation or polyaddition reactions are now readily synthesized by an efficient and logical multistep route with high degrees of purity.

Inorganic Polymer Science

In contrast to organic polymer science, the corresponding macromolecular chemistry of inorganic elements is at a much more primitive stage of development. Nevertheless, the creation of inorganic polymer structures offers the potential of new dimensions to the polymer-based materials, as illustrated by the relatively few thoroughly studied classes of these macromolecules (Chart 1).[1,2] For example, polysiloxanes **1**,[3] which contain long Si-O bonds, the absence of substituents on every other skeletal atom (oxygen), and a wide bond angle at oxygen, possess unique dynamic flexibility. This leads to materials that retain elasticity and do not become brittle even at very low temperature. In addition, Si-O bonds are stronger than C-C bonds and are more stable to oxidation and UV radiation. The P-N skeleton in polyphosphazenes **2** is also stronger, more oxidatively stable, and more conformationally stable than C-C bonds.[4] Poly(carbosilane)s **3** act as convenient precursors to silicon carbide ceramics via photolysis or thermolysis.[5] Due to the low energy σ–σ^* transitions, polysilanes **4** show appreciable electrical conductivity following doping. The delocalized σ electrons also lead polysilanes to be photosensitive and act as photoresist

materials.[6] Thus, with the development of inorganic polymers, access to new materials with interesting and useful properties might be achieved.

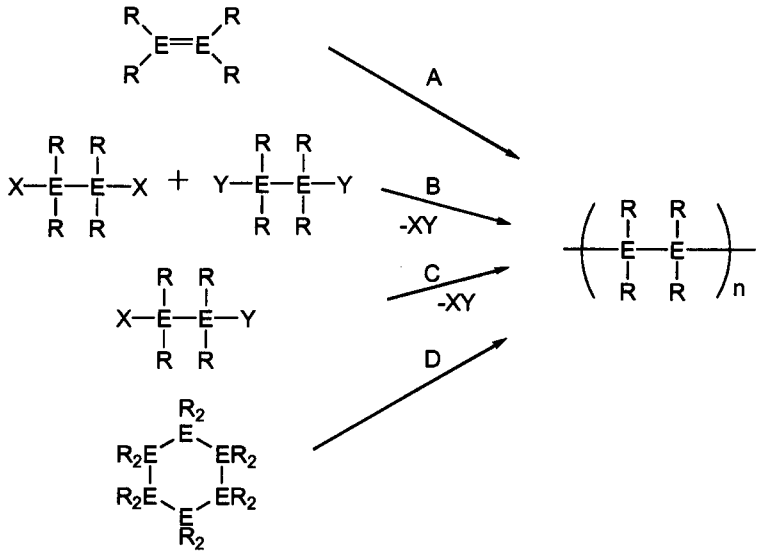
Chart 1



Synthetic Challenge of Inorganic Polymers

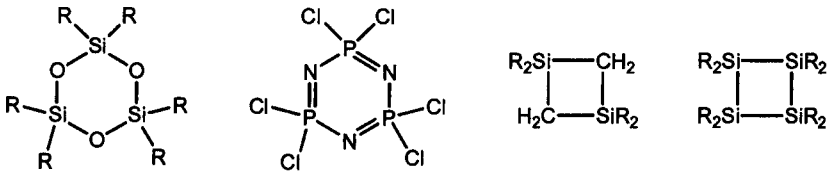
Despite the clear potential of this area, inorganic polymer science has received only sporadic bursts in the past. The synthesis of macromolecules utilizing inorganic elements provides a substantial synthetic challenge. Unlike organic chemistry, synthetic methodologies for the formation of bonds between inorganic elements are generally unpredictable and poorly developed. For example, traditional synthetic protocols that involve a chain-growth mechanism such as addition polymerization (Scheme 1, path A) are difficult to apply for inorganic polymer synthesis since multiply bonded inorganic monomer analogues are difficult to prepare. Their isolation requires the presence of sterically bulky group to prevent dimerization or oligomerization.[7] Since difunctional inorganic monomers are often so reactive that they are difficult to prepare with high purity. Indeed, a major

Scheme 1



problem in the past is that poorly defined impure difunctional monomers have been used for condensation polymerizations, which has led to the formation of only low molecular weight oligomeric products. Thus, the step-growth route (Scheme 1, B) has led to only the low molecular weight products. A promising variant of this type of condensation polymerization is to employ monomers with two groups, which can be eliminated from the same molecule (Scheme 1, C). This procedure has been successfully employed for the fabrication of polyphosphazenes **2**,[4] polysilanes **4** (Wurtz coupling)[6], and poly(phosphinoborane) (dehydro-coupling)[8] with high molecular weight ($M_n > 10^4$). The most well known and widely used current route to polysiloxanes **1**,[3] polyphosphazenes **2**,[4] poly(carbosilane)s **3**[5] is ring-opening polymerization (ROP) of the corresponding inorganic ring compounds (Chart 2), which is induced by heat, anionic or cationic initiators, or metal catalysts (Scheme 1, D). This methodology follows a chain-growth-type mechanism and circumvents the need for careful control of stoichiometry. With this in mind, the polymerization behavior of other inorganic rings, such as polysilanes **4**,[6] carbophosphazenes[9] and thiophophazenes,[10] has recently attracted attention. Inorganic homo- and heterocycle chemistry is one of the well-studied areas[11] and thus many potential ROP monomers are available.

Chart 2



Organoarsenic Chemistry

History[12]

Arsenic is a *metalloid*, which locates on the border line between metal compounds and non-metal compounds in the periodic table, but organoarsenic compounds are included in the "organometallic compound" classification, like the organic compounds of other metalloids such as boron, silicon, germanium, and tellurium. In this sense, an organoarsenic

compound, cacodyl (tetramethyldiarsine, $Me_2AsAsMe_2$), is the first organometallic compound to be synthesized.[13] The diarsine compound was synthesized in 1757 as a product of the reaction between arsenic trioxide and potassium acetate. During the late 1800s there was considerable interest in the synthesis of organoarsenic compounds that paralleled the heightened pursuit of synthetic organic chemistry. The discovery of the pharmacological activity of "Salvarsan" and its derivatives in 1910 led to a rapid expansion of the work on arsenic derivatives. Since 1960s less attention has been paid to chemotherapy roles and more to structures, stereochemistry and donor properties of organoarsenic compounds. Recently in the quest to develop viable single source precursors for Group 13 - 15 thin film technologies, the areas of arsenic-aluminum, arsenic-gallium and arsenic-indium have received significant attention and many new bonding and As-13 Group core systems have been explored. However, despite such a long and profound history of organoarsenic chemistry, the arsenic-containing polymer with well-defined structure had never been explored before the author's work.

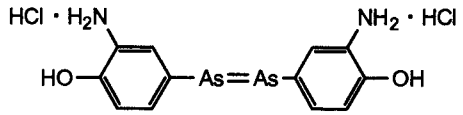
As-As Bonded Compounds

With regard to the E-E single bonds of later Group 15 elements (E = P, As, Sb, Bi), the bond energy becomes progressively weaker as the group is descended because of the increasing size of atoms and correspondingly poorer overlap between the larger orbitals [P-P: 201, As-As: 146, Sb-Sb: 121, Bi-Bi: not reported ($kJmol^{-1}$)].[14] This sequence accounts for the extensive number of known phosphorus-phosphorus and arsenic-arsenic bonded compounds in comparison to few examples of antimony and bismuth derivatives. Formation of R_2AsAsR_2 (R = Me (cacodyl), CF_3, or Ph) has been achieved in a variety of ways, including reduction of $R_2As(O)OH$ by H_3PO_2 and from reaction of R_2AsCl and R_2AsH.[15] The As-As bond in diarsines has considerable reactivity, which is illustrated by reaction with air,[16] sulfur,[17] alkali metal[18] and carbon-carbon multiple bonds.[19] The diarsines can also interact with transition metal compounds to form new complexes.[20] The ethylene analogue of arsenic, RAs=AsR, was synthesized and isolated by utilizing the bulky substitution such as $(Me_3Si)_3C$- and mesityl group.[21]

As mentioned above, Salvarsan and its derivatives had stimulated the development of

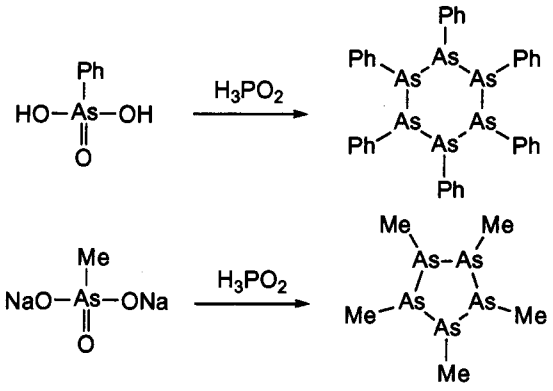
synthetic organoarsenic chemistry in 1910-1930s due to their chemotherapeutic effects. The structures of these compounds were thought in those days to be RAs=AsR, analogous to azobenzene (Chart 3). However, it is now known from X-ray crystallographic studies that "arsenobenzene" is actually a cyclic hexamer, *cyclo*-$(ArAs)_6$, and "arsenomethane" is a cyclic pentamer, *cyclo*-$(MeAs)_5$. In other words, it is the cyclooligoarsines[22] that made significant contribution to the development of organoarsenic chemistry in its early stage.

Chart 3. Proposed structure of Salvarsan



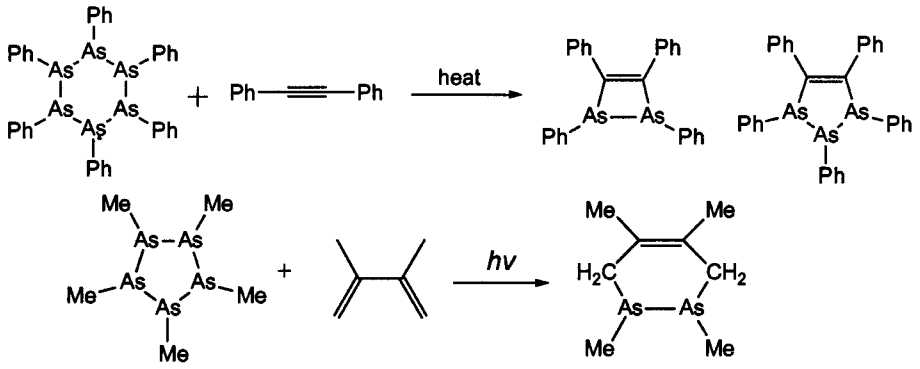
Most of the synthetic pathways to the cyclooligoarsines are analogous to those to diarsines. For example, the reduction of arsonic acids ($RAs(O)OH_2$) or its salt with H_3PO_2 has been most widely used (Scheme 2).[22] The reaction of primary arsine ($RAsH_2$) with dihaloarsine ($RAsCl_2$) has also been reported to yield cyclooligoarsines.[22] Six-membered arsenic ring is obtained exclusively with phenyl substitution and only five-membered ring is formed with methyl substitution. The substituent group on arsenic atom determines the ring structure while synthetic method has no effect.[22] Similarly to the diarsines, the arsenic-arsenic bond in cyclooligoarsines is readily cleaved by various reagents. The alkali metals cleave the cyclooligoarsines to give short chain polyarsines at low temperature; $M(RAs)_nM$, n = 3-5.[23] The reactions of cyclooligoarsines with elemental selenium result in the incorporation of the latter into the ring, to give five- or six-membered heterocycles.[24] A remarkable number of

Scheme 2



reactions between cyclooligoarsines with transition metals to result in unique forms of complexes had been investigated intensively.[20] The cleavage of cyclooligoarsines by unsaturated organic compounds serves as a useful procedure for preparing arsenic heterocycles (Scheme 3).[25] Compared to the reactions with inorganic compounds, relatively few examples of reactions with organic compounds were reported.

Scheme 3



Alternating Copolymerization

The exploitation of new polymeric materials is of going importance. Radical alternating copolymerization is one of the methodologies to create a novel polymeric material with well-defined structure.[26]

When two monomers M_1 and M_2 are mixed together in the presence of a radical initiator, there are a number of different ways in which the monomers combine. The possible structures of the product are

(i) a mixture of homopolymers of M_1 and M_2,

(ii) an *ideal* (or statistical) copolymer that contains a statistically random mixture of M_1 and M_2 units in the main chain, incorporated in the same proportion as that in the feed,

(iii) an alternating copolymer in which M_1 and M_2 units alternate along the backbone, e.g., ~$M_1M_2M_1M_2M_1M_2$~,

(iv) a copolymer with a structure intermediate to the extreme cases of (ii) and (iii).

Most radical copolymerizations lead to copolymers with intermediate structures (iv), the compositions of which are determined by the relative reactivities of the two monomers. For the synthesis of an alternating copolymer, one of the most precise controls of the propagating reaction is required in which only the cross-reactions ($M_1 \rightarrow M_2$ and $M_2 \rightarrow M_1$) are repeated alternatingly a number of times and with no homo-reactions ($M_1 \rightarrow M_1$ and $M_2 \rightarrow M_2$).

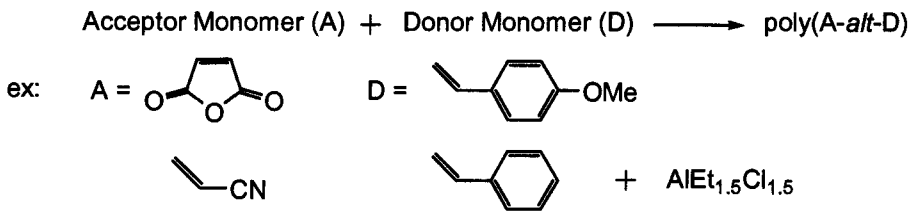
Many monomers which are reluctant to homopolymerize are often found to be capable of undergoing rapid copolymerization reactions with one another (Scheme 4).[27] If a strong electron donating monomer and a strong electron acceptor, such as *p*-methoxystyrene and maleic anhydride, are mixed together, a regular alternating copolymer is formed either by spontaneous initiation or more commonly in the presence of radical initiator, UV, or γ radiation. It is possible to divide the alternating systems identified into two broadly defined categories;

(i) systems in which there is alternating addition of comonomer during the reaction (terminal model),

(ii) systems where a copolymerization is thought to occur via a (1 : 1) charge transfer complex (CTC) (complex mechanism).

In the terminal model, the copolymerization is dominated by the cross reactions of free monomers caused by differences either in polarity or charge transfer reactions between the growing radical and the incoming comonomer. No free monomers are required in the complex mechanism and the chain is propagated by the "head-to-tail" homopolymerization of the charge transfer complex (CTC) of the donor-acceptor monomer pair. In practice, however, as neither mechanism is completely satisfactory, alternative approaches, which consider the simultaneous propagation through free monomers and the CTC, have gained favor.[28] The use of Lewis acids often enhances the alternating tendency for comonomer

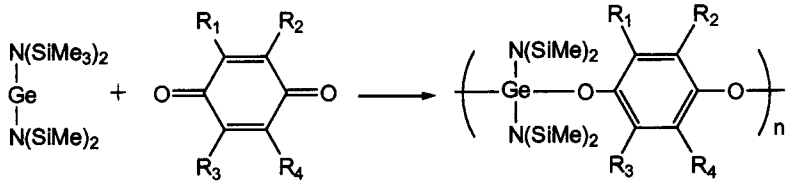
Scheme 4



pairs in which the relative strength of the electron-donor or acceptor is insufficient to result in pure (1 : 1) alternating copolymerization.[29]

As an exception to the two models, Kobayashi et al. reported the copolymerization which yielded the polymer having a tetravalent germanium unit and a *p*-hydroquinone unit alternatingly in the main chain by utilizing germylenes with bulky substitution and *p*-benzoquinone derivatives (Scheme 5).[30] By this copolymerization system they introduced a new concept of "oxidation-reduction alternating copolymerization" where a germylene acts as a reductant monomer and a *p*-benzoquinone derivative behaves as an oxidant monomer.

Scheme 5



Although exploration of new monomers and investigation of the mechanism for the radical alternating copolymerizations attracted considerable attention in 1970s-80s, there have been few developments of this area in these days.[31] Reevaluation of this synthetic methodology would bring about novel polymers with unique structures and features.

Survey of This Thesis

Conventional syntheses can produce polymers of restricted structures from which only well-known chemical and physical properties are predicted. The development of a new polymerization reaction makes it possible to create polymers having a unique structure which is difficult to construct by conventional procedures. As mentioned before, ring-opening polymerizations (ROP) of inorganic homocycles or heterocycles can produce inorganic polymers with characteristic properties. However, few attempts have been made to copolymerize the inorganic rings with organic monomers. As far as the author knows, only the copolymerization of cycloologosilane with *p*-benzoquinone derivatives using a transition metal catalyst is reported.[32] It is known that many kinds of cyclic inorganic compounds often cause element-element bond cleavage easily by heat, light, or a catalyst.[11] Thus, the

author thought that novel inorganic polymers with previously unattained structure could be constructed by expanding the scope of this relatively unexplored paradigm of polymer synthesis. In this thesis, the author describes the ring-collapsed radical alternating copolymerization (*RCRAC*) of inorganic homocycles of arsenic with acetylenic compounds to form the novel inorganic polymers, poly(vinylene-arsine)s (Scheme 6).

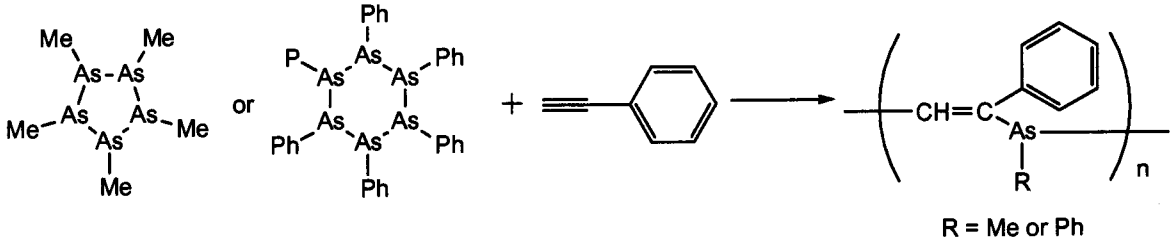
The present copolymerization system and the resulting polymers are characteristic in the following respects:

(i) This copolymerization is a rare example that utilizes an inorganic ring compound and organic unsaturated monomer. Needless to say, this is the first example of using cyclooligoarsine in polymer synthesis.

(ii) This copolymerization is a novel type of alternating copolymerization.[26] The arsenic homocycles do not act as monomers but oligomers: a five-membered ring is a pentamer and a six-membered ring is a hexamer. During the copolymerization, the ring structure (*cyclo*-$(RAs)_n$) breaks up into constitutional units (RAs), which are incorporated into the polymer backbone with no sequential parts. The high alternating character is accomplished by a unique mechanism that is different from "conventional" radical alternating copolymerizations. The difference of stability of As-As bonds between in the cyclic structure and in the open-chained state as well as the low homopolymerizability of acetylenic compounds bring about the "ring-collapsed" alternating copolymer but not "ring-opening" copolymer.

(iii) The obtained polymer, poly(vinylene-arsine), is the first example of the polymer having arsenic atoms in the main chain with well-defined structure. Though a few examples of arsenic containing polymer were reported, all of them were fairly unstable or

Scheme 6



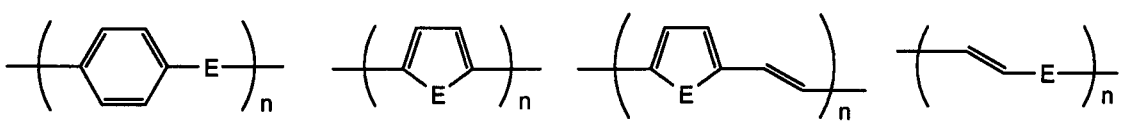
insoluble, and thus poorly characterized.[33]

(iv) The obtained polymer has a main chain structure in which the arsenic atoms are tethered by carbon-carbon double bond. The incorporation of main group element into unsaturated polymer main chain (Chart 4) appears to be a promising way to produce materials with useful properties. For example, heteroatom-including poly(phenylene)s such as poly(phenylene-oxide),[34] poly(phenylene-sulfide)[35] and polyaniline[36] have been industrially very important as engineering plastics or electric materials. Heteroaromatic polymers, such as polythiophene[37] and polypyrrole,[38] are also intensively investigated and have found wide applications. These polymers exhibit excellent mechanical properties, high stability, conductivity, energy storage ability and so on. However, heteroatom-including poly(vinylene)s, which might possess attractive properties, have never been reported because of the difficulties in the synthesis, except poly(vinylene-sulfide).[39]

Chapter 1 introduces a general concept of the synthetic methodology that the author develops in this thesis as an approach to novel inorganic polymers, and shows the synthesis of the first stable and soluble organoarsenic polymer, poly(vinylene-arsine), by a radical reaction between cyclooligoarsines and phenylacetylene in the presence of a radical initiator or UV irradiation. The characterization of the polymer by NMR spectroscopies and elemental analysis reveals the high alternating character of this copolymerization regardless of the monomer feed ratio. A copolymerization mechanism is proposed and supported by several experiments. Expansion of conjugation system and light-emitting property are illustrated by UV-vis absorption spectrum and fluorescence spectrum.

Chapter 2 demonstrates that ring-collapsed radical alternating copolymerization of the methyl-substituted cyclooligoarsine with phenylacetylene is induced spontaneously by simply mixing the two monomers. The copolymerization proceeds much more slowly than that in the presence of a radical initiator, which reflects the difference in the rate of the collapse of

Chart 4. Unsaturated Polymers Containing Main-Group Element



E = O, S, Se, NR, SiR_2

the ring structure. The gel permeation chromatography (GPC) analysis of the reaction mixture reveals the stepwise reaction character of the copolymerization.

In Chapters 3 and 4, the copolymerizations of cyclooligoarsines with acetylenic compounds having various kinds of substitutions are described. The measurement of the conversion rate of acetylenic compounds during the copolymerization by using gas chromatography (GC) suggests that an acetylene with substitution having more effective resonance effect consumes more quickly. This result supports that the formation of vinyl radicals by addition of arsenic radicals to acetylenic compounds is the rate-determining step in this copolymerization system. The optical properties of the polymers are tunable by changing the substituent of the acetylenic compound.

In Chapter 5, free radical terpolymerizations of pentamethylcyclopentaarsine, phenylacetylene, and various vinyl or butadienyl monomers are described. When a vinyl monomer is employed, the obtained polymer is a terpolymer which possesses two block segments of poly(vinylene-arsine) and the vinyl polymer. The obtained terpolymer shows fluorescent properties due to the poly(vinylene-arsine) block and the emission peak can be tuned by varying the monomer feed ratio. This terpolymerization system is unique in the respect that it gives a terpolymer with two kinds of blocks, one of which is an alternating copolymer and the other is a homopolymer, by the simple treatment of three kinds of monomers with a radical initiator. On the other hand, the terpolymerization using a butadienyl monomer forms a terpolymer which has random structure of arsenic-phenylacetylene unit and arsenic-butadiene unit.

In Chapter 6, the cross-linked poly(vinylene-arsine)s are synthesized by incorporating diethynylbenzene as a cross-linking agent in the radical polymerization of phenylacetylene and arsenic homocycle. In comparison with the linear poly(vinylene-arsine), the present cross-linked polymers show more improved film-forming properties, higher glass transition temperatures, and more red-shifted emissions, while the solubilities in organic solvents become lower. These properties can be controlled by varying the monomer feed ratio.

In Chapter 7, the methodology of ring-collapsed radical alternating copolymerization (*RCRAC*) is applied to a phosphorus ring compound. The 1 : 1 alternating copolymer, poly(vinylene-phosphine) is obtained by a radical reaction of a cyclooligophosphine with

phenylacetylene.

Chapter 8 deals with another example of the synthesis of novel arsenic-containing polymer utilizing arsenic radical. An organoarsenic cyclic compound with one arsenic-arsenic bond, 1,2,4,5-tetramethyltetrahydrodiarsenine, copolymerizes with various vinyl monomers in the presence of a radical initiator. This radical copolymerization proceeds under mild conditions and is, therefore, useful for the synthesis of novel polymers with arsenic linkages in the backbone and various functional groups as pendants.

Approaches toward novel arsenic- or phosphorus-containing polymers utilizing the reaction of arsenic or phosphorus radical are performed in this thesis. Though the function of phosphonyl radical as a radical initiator has been examined,[40] this is the first example of arsenic and phosphorus radical as propagating radicals. The methodology of *RCRAC* is available not only for arsenic rings but also for phosphorus rings, indicating the generality. The author believes that this method can be applied to other inorganic chain or ring compounds such as silicon, germanium, antimony, sulfur, selenium, and so on as described in Chapter 1 and will build up a new paradigm for the synthesis of inorganic polymers and heteroatom-containing polymers.

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Chapter 1

Synthesis of Poly(vinylene-arsine)s: Ring-Collapsed Radical Alternating Copolymerization (*RCRAC*) of Cyclooligoarsines with Phenylacetylene

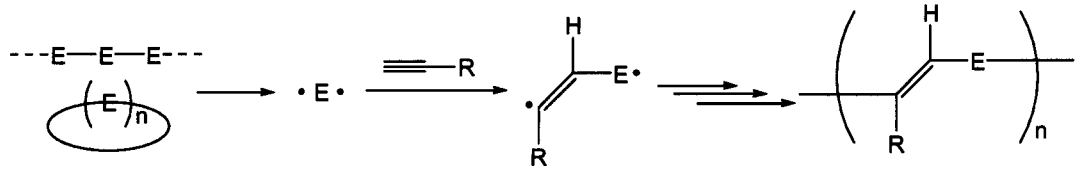
Abstract: Novel organoarsenic polymers, poly(vinylene-arsine)s, were synthesized by ring-collapsed radical alternating copolymerization (*RCRAC*) of cyclooligoarsines with phenylacetylene. The polymerization between pentamethylpentacycloarsine (**1a**) or hexaphenylhexacycloarsine (**1b**) with phenylacetylene (**2**) in the presence of a catalytic amount of AIBN (in benzene; refluxing; for 12 h) gave the corresponding poly(vinylene-arsine)s. The obtained polymers were soluble in common organic solvents such as THF, chloroform and benzene. From gel permeation chromatographic analysis (chloroform, PSt standards), the number-average molecular weights of the polymers from **1a** and **1b** were found to be 11500 and 3900, respectively. The structures of the polymers were supported by ^{1}H and ^{13}C-NMR spectroscopies. The corresponding polymer was also obtained by irradiation of a benzene solution of **1a** and **2** with xenon lamp at room temperature. The structure and the molecular weight of the polymer from **1b** were insensitive to the feed ratio of the monomers. This result indicates that the addition of the arsenic radical to phenylacetylene was a rate-determining step in the copolymerization.

Introduction

To develop new polymerization methods for heteroatom-containing unsaturated polymers is of considerable interest because such polymers show unusual properties. Among various types of such polymers, the simplest one is heteroatom-containing polyvinylenes, of which properties might be attractive. However, no example of these polymers has been reported except poly(vinylene-sulfide),[1] because of synthetic difficulties. This chapter describes a synthesis of poly(vinylene-arsine)s by ring-collapsed radical alternating copolymerization (*RCRAC*) of cyclooligoarsines with phenylacetylene.

Inorganic polymers or oligomers are known whose chains or ring skeletons are made up of only one inorganic element[2] such as silicon, germanium, phosphorus, arsenic, sulfur and selenium. These compounds often cause homolysis of element-element bonds by the stimulation such as light and heat. It is speculated that heteroatom-including polyvinylenes would be obtained by a radical copolymerization if atomic biradicals of the inorganic element obtained by the homolytic cleavage add to acetylenic compounds, and the resulting biradical adducts couple under head-to-tail manner (Scheme 1). Based on this concept, the author first chose organoarsenic ring compounds, cyclooligoarsines,[3] as inorganic oligomers. Cyclooligoarsines are prepared quite easily by reduction of corresponding arsonic acids or their salts with hypophosphorus acid. It is known that a methyl-substituted cyclooligoarsine is a five-membered ring and a phenyl-substituted one is a six-membered ring, because these ring structures are quite stable compared to other ring structures. Although a large number of studies have been made on the structural chemistry of cyclooligoarsines and their transition-metal complexes,[4] no radical reactions of cyclooligoarsines have been reported.[5] In this Chapter 1, cyclooligoarsines are regarded as monomers to prepare poly(vinylene-arsine)s by the radical copolymerization. It should be noted that this is the first soluble polymer containing arsenic atoms in the main chain.

Scheme 1



E = Si, Ge, P, As, S, Se, etc.

Results and Discussion

Synthesis and Characterization of Poly(vinylene-arsine)s. A typical polymerization procedure was conducted as follows (Scheme 2). Under a nitrogen atmosphere, a benzene solution of a catalytic amount of 2,2'-azobisisobutyronitrile (AIBN) was added to a refluxing solution of pentamethylpentacycloarsine (**1a**) and phenylacetylene (**2**) in benzene. After stirring for 12 h, the reaction mixture was poured into *n*-hexane to precipitate the product, which was purified three times by reprecipitation from benzene to *n*-hexane. After freeze-drying for 10 h, polymer **3a** was obtained as a bright-yellow powder. From gel permeation chromatographic analysis ($CHCl_3$, polystyrene standards), the number-average molecular weight of **3a** was estimated to be 11 500 (Table 1). In the case of using hexaphenylhexacycloarsine (**1b**) instead of **1a**, the corresponding poly(vinylene-arsine) (**3b**) was obtained as a bright-yellow powder. The relatively low yields are due to removal of

Scheme 2

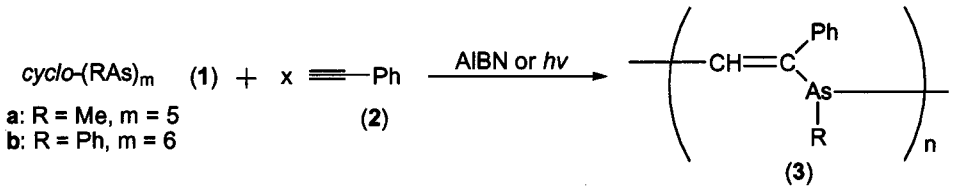


Table 1. Results of Copolymerizations

Run[a]	1	x[b]	Initiator	M_w[c]	M_n[c]	M_w/M_n[c]	Yield (%)[d]
1	*cyclo*-(AsMe)$_5$ (**1a**)	5.0	AIBN[e]	48700	11500	4.3	46
2	*cyclo*-(AsMe)$_5$ (**1a**)	5.0	*hν*[f]	11100	3400	3.3	48
3	*cyclo*-(AsPh)$_6$ (**1b**)	6.0	AIBN[e]	5600	3900	1.4	35
4	*cyclo*-(AsPh)$_6$ (**1b**)	6.0	*hν*[f]	No Polymer			
5	*cyclo*-(AsPh)$_6$ (**1b**)	3.0	AIBN[e]	5000	3500	1.4	34[g]
6	*cyclo*-(AsPh)$_6$ (**1b**)	1.0	AIBN[e]	5600	3800	1.5	trace
7	*cyclo*-(AsPh)$_6$ (**1b**)	12.0	AIBN[e]	7300	4100	1.8	17[g]

[a] Run 1, 3, and 5-7: in benzene at 350K. Run 2 and 4: in benzene at room temperature. [b] Molar ratio of **2** to **1**. [c] GPC ($CHCl_3$). Polystyrene standards. [d] Isolated yields after reprecipitation into *n*-hexane. [e] 3 mol% of AIBN was employed. [f] Xenon lamp. [g] Based on the molar amount of **2**.

low molecular weight products by reprecipitation. Both polymers were readily soluble in common organic solvents such as THF, chloroform and benzene.

Structural characterization of the polymers was provided by ^{1}H and ^{13}C NMR spectroscopies. In the ^{1}H NMR spectrum of **3a** (Figure 1), the integral ratio of two peaks in a vinyl region (6.1 to 6.4 ppm) confirmed that the trans isomer was predominantly obtained.[5a] From the peak area ratio of an aromatic (6.6 to 7.5 ppm) and a methyl region in the ^{1}H NMR and the elemental analysis, a copolymer composition of **3a** was nearly 1 : 1 (phenylacetylene : methylarsine). Analysis of **3a** by a ^{13}C NMR spectroscopy (Figure 2) showed only one sharp resonance for the methyl carbon at 11.6 ppm, suggesting that the arsenic in **3a** existed in a trivalent state and no arsenic-arsenic bond or no oxidized arsenic was present.[6,7] These results revealed that the copolymerization proceeded alternatingly.

After purification of the polymer **3b** by reprecipitation into *n*-hexane, the soluble part in *n*-hexane was investigated by GPC and ^{1}H NMR. It contained only low molecular weight

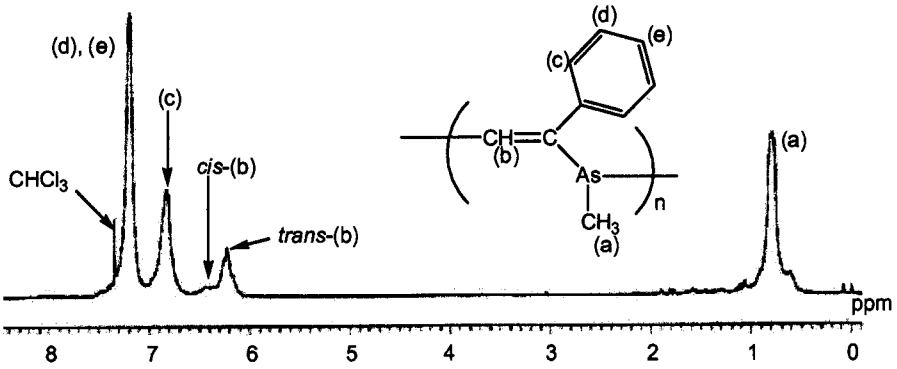


Figure 1. ^{1}H NMR spectrum of <u>3a</u> in $CDCl_3$.

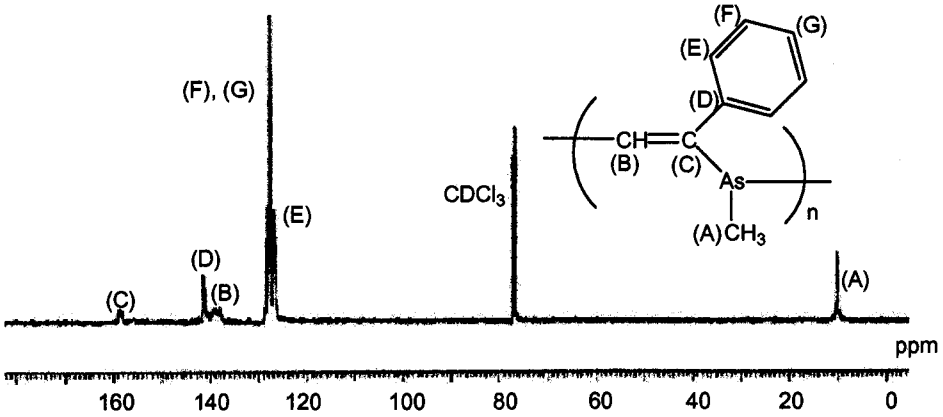


Figure 2. ^{13}C NMR spectrum of <u>3a</u> in $CDCl_3$.

materials by GPC. The ^{1}H NMR spectrum showed many peaks assigned to aromatic protons and a small broaden peak of vinyl proton. These results suggest that the *n*-hexane soluble part was mainly residual cyclooligoarsines and a small amount of low molecular weight oligomers. The consumption of **2** under the copolymerization condition with **1b** was monitored by gas chromatography (GC). The limit of the consumption of **2** was about 80 %.

The polymer **3a** was also obtained by irradiation of a benzene solution of **1a** and **2** with xenon lamp at room temperature (Table 1, Run 2). In Run 4 where **3b** and xenon lamp were employed, however, no polymer was obtained. In contrast to the case of using **1a**, the reaction mixture of Run 4 was heterogeneous because of poor solubility of **1b** at room temperature. Effective reaction did not proceed under a heterogeneous condition.

Stability of Poly(vinylene-arsine)s. To investigate the thermal stability of the obtained polymers, TGA analysis was carried out under nitrogen and air. The methyl-substituted poly(vinylene-arsine) **3a** showed a 10 % weight losses at 265 °C (under N_2) and 205 °C (under air), and the phenyl-substituted polymer **3b** showed them at 284 °C (under N_2) and 250 °C (under air), respectively. The poly(vinylene-arsine) with phenyl-substitution was thermally more stable than that with methyl-substitution. The glass transition temperatures (T_g) of **3a** and **3b** were 58.2 and 92.9 °C respectively determined by DSC analysis. Both of the resulting copolymers are stable in the solid state at room temperature. No decrease of the molecular weight or no change of the structure was observed even after exposing them to air for several months. In order to examine the stability toward air moisture and oxidation more precisely, the chloroform solution of **3a** was stirred in air atmosphere at 50 °C, and molecular weight change was monitored by GPC (Figure 3). The GPC analysis showed no decrease of the molecular weight after stirring for 24 h. The ^{1}H NMR spectrum of the recovered copolymer indicated no change of the polymer structure. In addition, after **3a** was stirred vigorously with 30 % H_2O_2 at 60 °C for 3 h, the ^{1}H-NMR spectrum and the GPC curve of the recovered polymer were the same as those for the starting polymer. These results suggest that the trivalent state of arsenic in the main chain was insensitive to the oxidation.

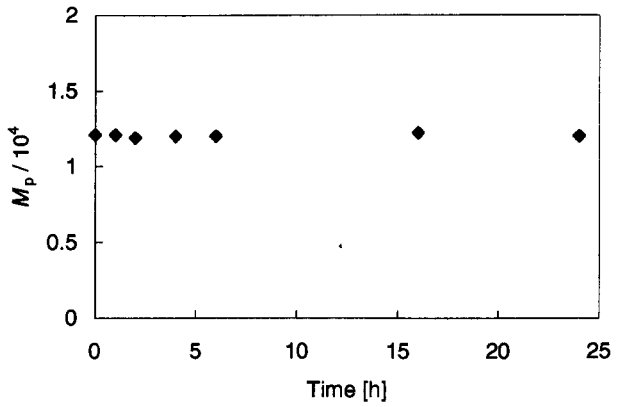
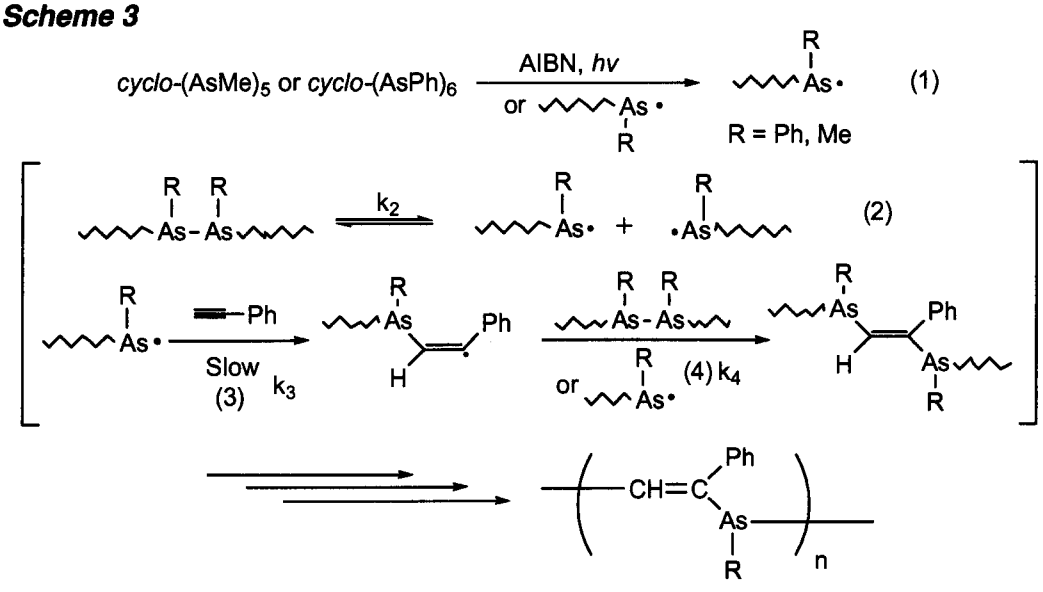


Figure 3. Molecular weight (M_p) change of **3a** in chloroform at 50 °C in air atmosphere monitored by GPC analysis.

Copolymerization Mechanism. It could be proposed here that the radical alternating copolymerization proceeds via following pathways (Scheme 3). First, AIBN or light cleaved the arsenic-arsenic bond of the cyclooligoarsines to produce arsenic radicals. Second, the homolysis of the other arsenic-arsenic bonds proceeded spontaneously due to their instability by the destruction of the quite stable five- or six-membered ring structure. In competition with this reaction, the arsenic radical added to phenylacetylene to give a vinyl radical. Next, the vinyl radical reacted immediately with the arsenic-arsenic bond or with the arsenic radical to form a new carbon-arsenic bond.

Scheme 3



To support the proposed mechanism for the polymerization, several experiments were carried out. When a suspension of phenyl-substituted cyclooligoarsine (**1b**) and **2** in benzene was refluxed in the absence of AIBN or *hv*, the corresponding poly(vinylene-arsine) was not produced. Because of the poor solubility of **1b** in benzene, the mixture of **1b** and benzene was heterogeneous at 78°C. After 3 mol% of AIBN was added, the mixture became homogeneous in a few tens of minutes. The stable six-membered ring structure should be collapsed to form open chain oligoarsines (and atomic biradical arsenic) under reflux condition with AIBN. When the homogeneous reaction mixture was cooled to room temperature, a large amount of the cyclooligoarsine was reproduced as white precipitates. These results indicate that the structure of **1b** undergoes homolytic cleavage by AIBN to produce arsenic radicals and the resulting arsenic radicals attacked to the remaining ring structure. The catalytic amount of AIBN was enough to cleave the arsenic-arsenic bonds. The consumption of **2** monitored by gas chromatography (GC) under the copolymerization condition with **1b** started after the reaction mixture was stirred for several minutes. These results suggest that the tertiary radicals derived from AIBN first reacted with the cyclooligoarsines followed by the reaction of the resulting arsenic radicals to phenylacetylene as shown in Scheme 3.

The copolymerization was carried out in different feed ratios (x = 1/6 - 12) of the two monomers, **1b** and **2** (Table 1, Run 5 – 7). In Run 5, the polymerization with 3 equivalents of **2** to **1b** gave a polymer which had the almost same molecular weight and the same structure. The polymerization with an equivalent of **2** to **1b** also gave a polymer with the almost same molecular weight and the same structure. If the rate of the arsenic-arsenic bond cleavage is comparable to the rate of the equation (3), some arsenic-arsenic bonds should be included in the polymer structure under the condition of Run 5 or 6, and the molecular weight of the polymer should be reduced due to labile As-As bonds in the structure during isolation. Thus, the addition rate (k_3) of the arsenic radical to phenylacetylene is much lower than the homolysis rate (k_2) of the arsenic-arsenic bond. When an excess amount of **2** was employed, the copolymer composition and the molecular weight of the polymer obtained were almost same as those of the polymer obtained in Run 3. If the reaction rate of the vinyl radical to the arsenic is comparable to the rate of the formation of the

vinyl radical, the resulting copolymer should have more vinylene units than arsenic units in the main chain. Therefore, the addition rate of the vinyl radical toward the arsenic-arsenic bonds or the arsine radicals should be much higher than the rate of equation (3). Thus, the addition reaction (equation (3)) should be a rate-determining step in the copolymerization. Due to the fast cleavage of the arsenic-arsenic bonds, the cyclooligoarsines are regarded as atomic biradical equivalents.

Optical Properties of Poly(vinylene-arsine)s. The UV-vis absorption spectrum of the polymer **3a** in chloroform showed small absorption at a visible region besides strong benzene-ring absorption at a UV region. The lower energy absorption edge was located at 550 nm. It is assumed that this lower energy absorption results from a delocalized n-π^* transition in the main chain.[8] The fluorescence emission spectrum of a dilute chloroform solution of **3a** showed an emission peak at 485 nm. In the excitation spectrum of **3a**, monitored at 485 nm, the absorption peak was observed at 396 nm corresponding to the n-π^* transition.

Summary

This chapter describes the synthesis of the novel organoarsenic polymers, poly(vinylene-arsine)s, by ring-collapsed radical alternating copolymerization (*RCRAC*) of the cyclooligoarsines with phenylacetylene. The present polymerization system should be regarded as a new example of radical alternating copolymerizations, in which the arsenic ring structure is disrupted into constitutional unit (RAs, R = Me or Ph) and the unit was incorporated into the polymer backbone with no sequential parts. It is believed that the present method provides a unique mechanism for designing new heteroatom-containing polymers, especially heteroatom-containing polyvinylenes.

Experimental Section

Materials and Instruments. Unless otherwise noted, all reagents and chemicals were purchased from Wako Pure Chemical Industries, Ltd. Phenylacetylene (**2**) was purchased from Aldrich and distilled under reduced pressure. Benzene was dried over CaH_2, distilled and bubbled with a stream of nitrogen before use. *n*-Hexane (water < 30 ppm), was used

without further purification. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from methanol. ^{1}H-NMR spectra were recorded on a 270 MHz JEOL-JNM-GX270 NMR spectrometer. ^{13}C-NMR spectra were recorded on a 67.5 MHz JEOL-JNM-GX270 NMR spectrometer. Gel permeation chromatographic analysis was carried out on a Shodex K-803 by using $CHCl_3$ as an eluent after calibration with polystyrene standards. Gas chromatography (GC) analyses were carried out on a SHIMADZU GC-17A using helium gas as a carrier gas. Thermogravimetric analysis (TGA) was performed on a TG/DTA6200, Seiko Instruments Inc. at the rate of 10 °Cmin^{-1}. Differential scanning calorimetry (DSC) thermograms were obtained with a DSC200, Seiko Instruments Inc., with the heating rate of 10 °Cmin^{-1} under a nitrogen atmosphere.

Cyclooligoarsines. **1a** and **1b** were prepared according to ref. 6 and 9, respectively. **1a**. ^{1}H-NMR (δ, ppm) 1.63, 1.64, 1.67 (lit.[6] 1.62, 1.63, 1.66). **1b**. mp 208 – 211 °C (lit.[9] mp 204 – 208 °C).

Polymerization. A typical experimental procedure is as follows. Under a nitrogen atmosphere, a benzene solution (1 mL) of AIBN (0.24 g, 1.5 mmol) was added to a refluxing solution of pentamethylcyclopentaarsine (**1a**) (4.38 g, 9.74 mmol) and phenylacetylene (**2**) (4.96 g, 48.6 mmol) in benzene (30 mL). After stirring for 12 h, the reaction mixture was poured into *n*-hexane to precipitate the product, which was purified three times by reprecipitation from benzene to *n*-hexane. After freeze-drying for 10 h, the corresponding polymer **3a** was obtained as a bright-yellow powder (4.35 g, 22.6 mmol) in 46 % yield.

3a. ^{1}H-NMR (δ, ppm): 0.78 (As-CH_3), 6.21 (*(E)*-C=CH), 6.43 (*(Z)*-C=CH), 6.83 (ArH_o), 7.19 (ArH_m, ArH_p). ^{13}C-NMR (δ, ppm): 10.7 (As-CH_3), 126.0-129.0 ($C_{Ar}H_o$, $C_{Ar}H_m$, $C_{Ar}H_p$), 137.9-139.7 (C=*C*H), 141.4 (C_{Ar}-C), 158.9 (*C*=CH). Anal. Calcd for $[C_8H_6(CH_3As)_{1.07}]_n$: C, 54.9; H, 4.7. Found: C, 54.3; H, 4.8.

3b. ^{1}H-NMR (δ, ppm): 6.24 (C=CH), 6.3-7.6 (ArH). ^{13}C-NMR (δ, ppm): 127.7-130.1, 133.7-134.3 ($C_{Ar}H$), 138.0-139.8 (*C*H=C), 141.5-142.0 (C-C_{Ar} ,As-C_{Ar}), 161.1 (CH=*C*). Anal. Calcd for $[C_8H_6(C_6H_5As)_{1.2}]_n$: C, 64.2; H, 4.3. Found: C, 63.3; H, 4.3.

Stability of 3a toward Air. A chloroform solution (10 mL) of **3a** (0.54 g) was stirred for 24 h at 50 °C. During the stirring, a small amount of the solution was siphoned, diluted with chloroform, and analyzed by the GPC, suggesting no decrease of the molecular weight.

The ^{1}H NMR spectrum of the polymer recovered after the stirring was identical with that of the starting polymer.

Stability of 3a toward Oxidation. A benzene solution (3 mL) of **3a** (0.10 g) was stirred at 60 °C for 3 h. After removal of the solvent the recovered polymer was analyzed by GPC and ^{1}H NMR. No significant change was observed.

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Chapter 2

Spontaneous Ring-Collapsed Radical Alternating Copolymerization (*RCRAC*) of Homocyclic Arsenic Compound and Phenylacetylene

Abstract: Under a nitrogen atmosphere at room temperature, pentamethylcyclopentaarsine (*cyclo*-$(MeAs)_5$) transferred to an insoluble ladder structured oligoarsine, which was formed by spontaneous cleavage of the arsenic-arsenic bond of the ring structure and subsequent stacking of the open-chain oligoarsine. The formation of the precipitate was accelerated by 2,2'-azobisisobutyronitrile (AIBN) or an irradiation by incandescent lamp. The ring structure of hexaphenylcyclohexaarsine (*cyclo*-$(PhAs)_6$) was collapsed by AIBN in refluxing benzene, while it remained intact in the absence of AIBN. Without any added catalyst or radical initiator at 25 °C, *cyclo*-$(MeAs)_5$ was copolymerized spontaneously with phenylacetylene (PA) in chloroform to give a novel organoarsenic polymer having a methylarsine (MeAs) unit and a vinylbenzene unit alternatingly in the main chain, -$[AsMe\text{-}CH{=}CPh]_n$-. The spontaneous copolymerization of *cyclo*-$(MeAs)_5$ and PA in various monomer feed ratios was also carried out in chloroform at 25 °C and, in all cases, gave the alternating copolymer with MeAs and PA units. While the excess amount of PA was found to remain unchanged after the completion of the reaction, the excess amount of a repeating unit of *cyclo*-$(MeAs)_5$ against PA decreased the molecular weight and the yield of the obtained polymers in comparison with those in the equivalent case. The rate of monomer consumption during the copolymerization was followed by a gas chromatography (GC) analysis and the increase of the molecular weight of the resulting copolymer was monitored by GPC measurement. These analyses revealed that this system was step-reaction polymerization. The consumption of PA during the copolymerization with *cyclo*-$(MeAs)_5$ using AIBN was much faster compared to the case without AIBN.

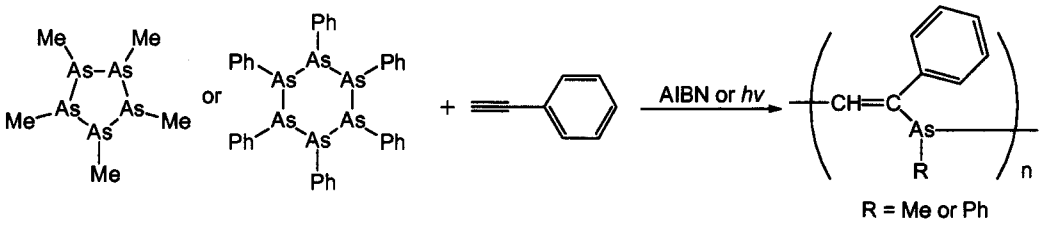
Introduction

Many monomers which are reluctant to homopolymerize are often found to be capable of undergoing rapid copolymerization reactions with one another.[1] If a strong electron donating monomer and a strong electron acceptor, such as *p*-methoxystyrene and maleic anhydride, are mixed together, a regular alternating copolymer is formed either by spontaneous initiation or more commonly in the presence of a radical initiator, UV, or γ radiation. The mechanism to regulate the comonomer sequence alternatingly is roughly divided into two models; the terminal model and the complex mechanism. In the terminal model, the copolymerization is dominated by the cross reactions of free monomers caused by differences either in polarity or charge transfer reactions between the growing radical and the incoming comonomer. No free monomers are required in the complex mechanism and the chain is propagated by the "head-to-tail" homopolymerization of the charge transfer complex (CTC) of the donor-acceptor monomer pair. In practice, however, as neither mechanism is completely satisfactory, alternative approaches, which consider the simultaneous propagation through free monomers and the CTC, have gained favor. As an exception to the two models, Kobayashi et al. reported the copolymerization which yielded the polymer having a tetravalent germanium unit and a *p*-hydroquinone unit alternatingly in the main chain by utilizing germylenes and *p*-benzoquinone derivatives.[2] By this copolymerization system they introduced a new concept of "oxidation-reduction alternating copolymerization" where a germylene acts as a reductant monomer and a *p*-benzoquinone derivative behaves as an oxidant monomer.

The preceding chapter the author describes the synthesis of poly(vinylene-arsine)s by a radical reaction between cyclic organoarsenic compound, such as pentamethylcyclopentaarsine (*cyclo*-$(MeAs)_5$) or hexaphenylcyclohexaarsine (*cyclo*-$(PhAs)_6$), and phenylacetylene (PA) using 2,2'-azobisisobutyronitrile (AIBN) as a radical initiator (Scheme 1).[3] This is a novel type of radical alternating copolymerization, in which the arsenic ring compound fell into pieces and the arsenic unit was incorporated into the polymer backbone with no arsenic-arsenic bonds. Therefore the author has named this copolymerization system "ring-collapsed radical alternating copolymerization (*RCRAC*)".

The obtained poly(vinylene-arsine) is the first example of the soluble polymer containing arsenic atoms in the main chain with well-defined structure.

Scheme 1



Though the history of the organoarsenic homocycles[4] dates back at least to the synthesis of *cyclo*-$(PhAs)_6$ by Michaelis and Schulte in 1881[5] and the chemotherapic effects of "Salvarsan" and their derivatives were discovered[6] and studied intensively in the early part of the 20th century, relatively only a little has been developed of reactions of the organoarsenic homocycles with organic compounds[7] compared to the extensive studies on coordination chemistry of them as ligands in transition metal complexes.[8] No radical reactions of the cyclooligoarsines had been reported before the author's study. Revaluation of the organoarsenic homocycles would open a unique chemistry.

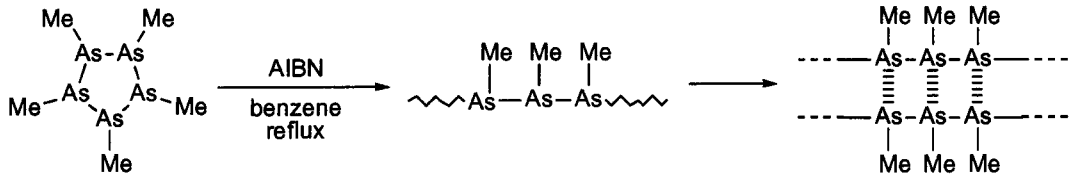
This chapter describes the detail studies of *RCRAC* of the cyclooligoarsines with phenylacetylene as well as the reactivity of the cyclooligoarsines. Although the phenyl-substituted arsenic ring compound showed no reaction with phenylacetylene without AIBN in refluxing benzene, the methyl-substituted arsenic ring is found to react with phenylacetylene in the absence of any radical initiators or catalysts to produce the corresponding poly(vinylene-arsine) at 25 °C. The difference of the copolymerization behavior between with and without AIBN is also a subject of this chapter.

Results and Discussion

Synthesis and Reactions of Cyclooligoarsines. To examine the copolymerization mechanism, especially the spontaneous cleavage of the arsenic-arsenic bonds of the cyclooligoarsines, here discusses the formation and reactions of the cyclooligoarsines. The methyl-substituted cyclooligoarsine, *cyclo*-$(MeAs)_5$, was synthesized by the reduction of

sodium methylarsonate with hypophosphorus acid.[12] The five-membered arsenic ring was obtained exclusively, suggesting that this ring structure is stable compared to other forms containing arsenic-arsenic bonds. The obtained *cyclo*-$(MeAs)_5$ is yellow liquid with high viscosity. After *cyclo*-$(MeAs)_5$ was left under a nitrogen atmosphere at 25 °C for several days, a purple black precipitate appeared, which could be easily removed by filtration under a nitrogen atmosphere. The resulting precipitate was insoluble in any solvent and fuming in the air, and, according to the literature,[9] must be a linear poly(methylarsine) with a ladder structure. The arsenic-arsenic bond of the ring compound was cleaved spontaneously, and then the open-chain oligoarsine stacked with each other to form the ladder structure (Scheme 2). Solutions of *cyclo*-$(MeAs)_5$ in organic solvents such as benzene, toluene, and chloroform also produced the purple-black precipitates after standing at 25 °C for several days. The formation of the precipitate was accelerated by heating in the presence of AIBN or by the irradiation with an incandescent lamp. Under these conditions, a large quantity of the precipitate was obtained within a few hours, suggesting that the cleavage of the arsenic-arsenic bonds of *cyclo*-$(MeAs)_5$ was promoted by AIBN or *hv*. The precipitate showed no reaction due to the low solubility when a benzene solution of PA and a catalytic amount of AIBN was added to the precipitate and the mixture was stirred at 78 °C for several hours.

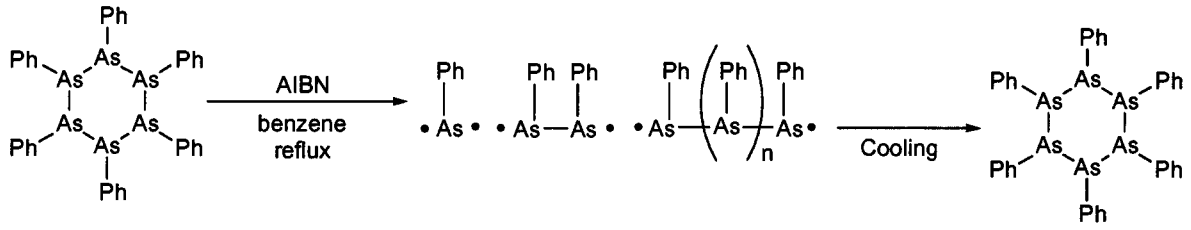
Scheme 2



The reduction of phenylarsonic acid with hypophosphorus acid yielded the six-membered arsenic ring compound[13] but no other rings or chains of arsenic were formed by this reduction. The phenyl-substituted cyclooligoarsine, *cyclo*-$(PhAs)_6$, was obtained as a pale yellow crystal after recrystallization from chlorobenzene. The crystal showed poor solubility in benzene. When *cyclo*-$(PhAs)_6$ was treated with 3 mol% of AIBN in refluxing benzene, the heterogeneous reaction mixture became clear within 30 minutes. The stable ring structure

was collapsed and open-chain arsenic oligomers or arsenic atomic biradicals might be formed in the solution (scheme 3). By cooling the clear solution to room temperature, *cyclo*-$(PhAs)_6$ was reproduced as a light yellow powder. The catalytic amount of AIBN was enough to transparentize the mixture, in other words, to collapse all of the stable six-membered ring structure, suggesting that the produced arsenic radial also contributed to the destruction of *cyclo*-$(PhAs)_6$. In contrast to *cyclo*-$(MeAs)_5$, *cyclo*-$(PhAs)_6$ was stable at room temperature in the air atmosphere in the solid state, and showed no reaction even in refluxing benzene for several hours.

Scheme 3



Spontaneous Alternating Copolymerization of *cyclo*-$(MeAs)_5$ with PA. The arsenic ring compound with methyl-substitution, *cyclo*-$(MeAs)_5$, reacted with PA in chloroform at 25 °C in the absence of any radical initiators or catalysts to produce the corresponding poly(vinylene-arsine) in moderate yield (Table 1, Run 1). The copolymerization was initiated simply by mixing chloroform solution of *cyclo*-$(MeAs)_5$ and PA. The resulting copolymer was purified by reprecipitation from toluene to *n*-hexane. The copolymer showed a single peak on the GPC trace. The number-average molecular weight of the copolymer was estimated to be 11 100 by the GPC analysis (vs polystyrene standards). The structure of the resulting copolymer was determined by ^{1}H NMR and ^{13}C NMR spectra. Both spectra were identical with those of the poly(vinylene-arsine) prepared using a catalytic amount of AIBN as a radical initiator in Chapter 1. The ratio of the peak areas of the vinyl proton and the methyl proton in the ^{1}H NMR spectrum showed that the copolymer consisted of 1 : 1 unit of methylarsine (MeAs) and PA. The ^{13}C NMR spectrum exhibited a single peak attributable to the methyl carbon at 10.3 ppm, suggesting that the obtained copolymer possessed no arsenic-arsenic bonds or oxidized arsenic in the main chain.

Table 1. Copolymerization of *cyclo*-$(MeAs)_5$ with PA: Effect of Solvent and Reaction Temperature[a]

			resulting polymer		
Run	solvent	temp (°C)	yield (%)[b]	M_n[c]	M_w/M_n[c]
1	chloroform	25	64	11 100	2.1
2	chloroform	0	56	9 900	2.1
3	chloroform	50	52	8 800	1.9
4	toluene	25	60	13 000	2.4
5	toluene	100	38	4 000	1.6
6[d]	toluene	25	63	11 500	2.1
7	benzene	25	59	11 300	2.2
8	diethyl ether	25	45	7 400	2.1
9	THF	25	58	15 000	2.8
10[d]	none	25	41	600	3.4

[a] Copolymerization was carried out with 1 : 5 feed molar ratio of *cyclo*-$(MeAs)_5$ and PA for 12 h under nitrogen. [b] Isolated yield after reprecipitation from toluene into *n*-hexane. [c] Determined by GPC (chloroform, polystyrene standards). [d] Copolymerization was carried out in a light resistant container. The reaction mixture was solidified within 15 minutes and the reaction was ceased.

After the copolymerization of *cyclo*-$(MeAs)_5$ with PA in chloroform was carried out for 12 h, the reaction mixture was analyzed by GPC before the reprecipitation (Figure 1). Besides a peak assigned to the poly(vinylene-arsine) with high molecular weight, the GPC chart shows two peaks in the region of the molecular weight of several hundreds. By the recycling HPLC analysis using chloroform as an eluent, it was revealed that both of the two peaks in the lower molecular weight region consisted of several peaks.[10] Since the compounds accounting for the two peaks were soluble in *n*-hexane and the polymeric material was not, they were separated from each other by pouring the reaction mixture after the copolymerization into *n*-hexane. The low molecular weight compounds were stirred in toluene at 25 °C for 12 h, and then no polymer was obtained. This result suggests that the polymer with high molecular weight was *not* formed via the compounds responsible for these peaks. Similar peaks were also observed in the GPC trace when a catalytic amount of

AIBN was employed as a radical initiator in the copolymerization. The formation of these compounds decreases the isolated yield of the polymer with high molecular weight.

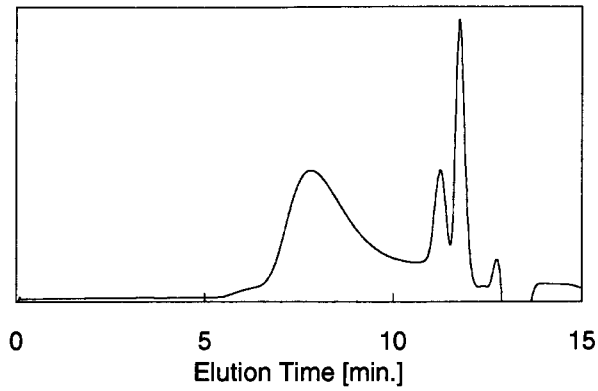


Figure 1. GPC trace (chloroform) of the reaction mixture after the copolymerization of *cyclo*-(MeAs)$_5$ with PA in chloroform at 25 °C in the absence of AIBN before the reprecipitation.

Table 1 summarizes the effect of solvents and temperature on the copolymerization of *cyclo*-(MeAs)$_5$ with PA. Various solvents were found usable for affording copolymers with number-average molecular weight of more than ten thousands in moderate yields at 25 °C (Table 1, Run 1, 4, 7, 9). The molecular weight and yield of the poly(vinylene-arsine) decreased when the copolymerization was carried out at 100 °C in toluene (Table 1, Run 5), probably because chain-transfer reactions took place more often at higher reaction temperature. The use of diethyl ether also gave the copolymer with the same structure and slightly decreased molecular weight although the reaction system was heterogeneous during the copolymerization because of the poor solubility of the poly(vinylene-arsine). The reaction of *cyclo*-(MeAs)$_5$ with PA in toluene at room temperature was carried out in a light resistant container (Table 1, Run 6) and produced the polymer with almost same molecular weight and same structure as those in Run 4. The possibility of light energy to initiate the copolymerization is excluded by this result. The reaction between *cyclo*-(MeAs)$_5$ and PA without any solvent afforded a transparent yellow solid in 15 minutes (Table 1, Run 10). The obtained solid contained the monomers and oligomer with low molecular weight, which was characterized by ^{1}H NMR spectroscopy and GPC analysis.

The treatment of *cyclo*-$(PhAs)_6$ with PA in toluene without AIBN at 25 °C or 60 °C for several hours resulted in no polymer and the recovery of the monomers. The poor solubility of *cyclo*-$(PhAs)_6$ in toluene is attributable as described above.

Spontaneous Copolymerization in Various Monomer Feed Ratios. The copolymerization of *cyclo*-$(MeAs)_5$ with PA was conducted in chloroform at 25 °C in various monomer feed ratios (Table 2). In all cases the copolymerization resulted in the corresponding alternating copolymer, poly(vinylene-arsine). Thus, the 1 : 1 alternating structure of MeAs and PA is controlled very strictly under a wide variety of copolymerization conditions. These results can be explained by the mechanism proposed in Chapter 1. Since the vinyl radical reacts with arsenic-arsenic bond or arsenic radical immediately after the production due to the instability, almost all of the propagating radical in the copolymerization system are arsenic radical and the concentration of the vinyl radical is extremely low. Thus, the vinyl radical never reacts with another vinyl radical. It rarely attacks PA either because of the low homopolymerizability of PA. These are also the case for Run 4 and 5 in which the excess amount of PA was employed. Therefore, the resulting copolymers have no consecutive PA units in the main chain in all the cases. The other propagating radical, the arsenic radical, can cause the recombination reaction as a termination.

Table 2. Copolymerization of *cyclo*-$(MeAs)_5$ with PA in the Absence of AIBN : Effect of the Feed Ratios of Monomers

	feed ratio	resulting polymer		
Run[a]	MeAs[b] : PA	M_n[c]	M_w/M_n[c]	Yield (%)[d]
1	1 : 0.33	5 200	2.6	17[e] (32)[f]
2	1 : 0.67	5 200	2.7	42[e] (52)[f]
3	1 : 1	11 100	2.1	64[e]
4	1 : 1.5	13 100	2.3	52[e] (65)[g]
5	1 : 1.5	11 200	2.1	30[e] (61)[g]

[a] Copolymerizations were carried out in chloroform at 25 °C for 12 h. [b] MeAs represents methylarsine (CH_3As). [c] Estimated by GPC analysis in chloroform on the basis of polystyrene standards. [d] Isolated yield after reprecipitation from toluene to methanol. [e] (weight of polymer)/(total weight of monomers). [f] Based on the molar amount of PA. [g] Based on the molar amount of *cyclo*-$(MeAs)_5$.

The resulting diarsenic linkage, however, is unstable and can bring about its homolytic cleavage to reproduce the arsenic radical as a propagating end-group. Consequently, even when the excess amount of *cyclo*-$(MeAs)_5$ was employed, the copolymerization yielded the copolymer with no consecutive MeAs units in the backbone.

While the excess amount of PA (Table 2, Run 4 and 5) was found to remain unchanged after the completion of the reaction, the excess amount of MeAs (Table 2, Run 1 and 2) decreased the molecular weights and yields of the obtained polymers in comparison with those in the equivalent case (Table 2, Run 3). Since almost all the propagating radical are the arsenic radical even in the case that the excess PA was employed, the copolymerization in Run 4 and 5 proceeded comparably with the equivalent case. When the less amount of PA than that of MeAs was employed, all PA was consumed before the sufficient growth of the copolymer chain. Thus, the copolymerization in Run 1 and 2 yielded the alternating copolymer with low molecular weight, and hence in low yield after the removal of the oligomer by reprecipitation.

Alternating Copolymerization of *cyclo*-$(MeAs)_5$ or *cyclo*-$(PhAs)_6$ with PA in the Presence of a Radical Initiator. The copolymerization of *cyclo*-$(MeAs)_5$ with PA using a catalytic amount of AIBN produced the corresponding poly(vinylene-arsine) as reported in Chapter 1. Here conducted the copolymerizations of *cyclo*-$(MeAs)_5$ and PA in various monomer feed ratios with 1.5 mol% of AIBN in toluene at 60 °C for 2 h. Table 3 summarizes the results of the copolymerizations. The molecular weights and yields were measured after the purification of the resulting polymers by reprecipitation into *n*-hexane. Similarly to the copolymerization without AIBN, the excess amount of PA had no influence on the obtained polymer (Table 3, Run 4 and 5) while the excess amount of MeAs yielded the copolymer with low molecular weight and in low yield (Table 3, Run 2) or no polymeric material (Table 3, Run 1). By the characterization with ^1H and ^{13}C NMR spectra, the obtained copolymers were the poly(vinylene-arsine) in all the cases.

The difference in the production rate of the arsenic radicals with and without AIBN affected the results of the copolymerization of *cyclo*-$(MeAs)_5$ with PA fed in the excess amount of MeAs. In the feed ratio of MeAs : PA = 1 : 0.67, the copolymerization without AIBN (Table 2, Run 2) yielded the alternating copolymer with higher molecular weight in

Table 3. Copolymerization of *cyclo*-$(MeAs)_5$ with PA in the Presence of AIBN : Effect of the Feed Ratios of Monomers

	feed ratio	resulting polymer		
Run[a]	MeAs : PA	M_n[b]	M_w/M_n[b]	Yield (%)[c]
1	1 : 0.33			0[d]
2	1 : 0.67	3 900	1.7	21[d] (26)[e]
3	1 : 1	11 300	1.8	50[d]
4	1 : 1.5	12 200	1.4	42[d] (53)[f]
5	1 : 3	11 000	2.4	26[d] (54)[f]

[a] Copolymerizations were carried out in toluene at 60 °C for 2 h. [b] Estimated by GPC analysis in chloroform on the basis of polystyrene standards. [c] Isolated yield after reprecipitation from toluene to methanol. [d] (Weight of polymer) / (total weight of monomers). [e] Based on the molar amount of PA. [f] Based on the molar amount of *cyclo*-$(MeAs)_5$.

higher yield than those of the copolymer produced with AIBN (Table 3, Run 2). While the reaction without AIBN in the feed ratio of MeAs : PA = 1 : 0.33 (Table 2, Run 1) produced the copolymer, the treatment of them in the same feed ratio with AIBN yielded no precipitation when the reaction mixture was poured into *n*-hexane (Table 3, Run 1). In the presence of AIBN, the concentration of the arsenic radical became high in a few minutes, and hence all PA was consumed at the early stage of the copolymerization, yielding the low molecular-weight oligomer of the vinylene-arsine structure. In the absence of AIBN, on the other hand, the concentration of the arsenic radical was low at the initial stage, and hence during that period the growth of the polymer chain was accomplished though it was insufficient compared to the equivalent case.

The copolymerization of *cyclo*-$(PhAs)_6$ with PA in various monomer feed ratios using AIBN was described in Chapter 1 and resulted in the copolymers having a 1 :1 alternating structure with the almost same molecular weights in the similar yields. The excess amount of the phenylarsine unit (PhAs) had no effect on the obtained copolymer in contrast to the case of MeAs. In the case of *cyclo*-$(PhAs)_6$, the concentration of the propagating arsenic radical kept low compared to the case of *cyclo*-$(MeAs)_5$ due to the poor solubility of *cyclo*-$(PhAs)_6$. It took about 30 minutes after the copolymerization was initiated by adding AIBN to make the reaction mixture homogeneous, in other words, to collapse all the insoluble

ring structure producing the arsenic radical. Therefore, the same copolymer as in the equivalent case was obtained even when the excess amount of PhAs was employed.

Emulsion Polymerization. The methyl-substituted cyclooligoarsine, *cyclo*-$(MeAs)_5$, afforded the corresponding poly(vinylene-arsine) by the copolymerization with PA using water as reaction media. The copolymerization was carried out under a nitrogen atmosphere using water, *cyclo*-$(MeAs)_5$, PA, sodium lauryl sulfate as an emulsifier, and potassium peroxodisulfate as a water-soluble radical initiator in the weight ratio of 2 : 1 : 0.1 : 0.01. After vigorous stirring for 8 h at 80 °C, the obtained polymer latex was poured into methanol and the precipitate was washed by methanol. The obtained polymer was purified by reprecipitation into *n*-hexane to yield the corresponding poly(vinylene-arsine) as a yellow-white powder (yield 27%). The number-average molecular weight (M_n) of the copolymer was 4 700 with the polydispersity index (M_w/M_n) of 4.1. ^{1}H-NMR and ^{13}C-NMR spectra were employed to support the structure of the polymer. The fact that the copolymerization proceeded in the presence of water excludes the possibility that ionic species contribute to the propagation of the copolymerization.

Gas Chromatography (GC) and Gel Permeation Chromatography (GPC) Analysis. The GC study of the copolymerization system was carried out to investigate the consumption rate of PA. The spontaneous alternating copolymerization of *cyclo*-$(MeAs)_5$ with PA in chloroform at 25 °C was conducted in the presence of mesitylene as a standard material. During the copolymerization a small amount of reaction mixture was siphoned, diluted with chloroform, and analyzed by the GC. The conversion of PA was calculated by the peak area ratio of PA and mesitylene. The conversion rate of PA during the copolymerization with *cyclo*-$(MeAs)_5$ in toluene at 60 °C in the presence of 3 mol% of AIBN was also analyzed by the GC. Both of the results are plotted in Figure 2. The spontaneous copolymerization took nearly 4 h to convert 90 % of PA, while the conversion of PA reached 100 % within 40 minutes by the reaction with *cyclo*-$(MeAs)_5$ in the presence of AIBN. The GC analysis during the copolymerization without AIBN at 60 °C in toluene was also performed and exhibited no significant difference with the spontaneous copolymerization in chloroform at 25 °C. Effect of the reaction temperature on the rate of the copolymerization was negligible. The large difference in the conversion rate of PA between with and without

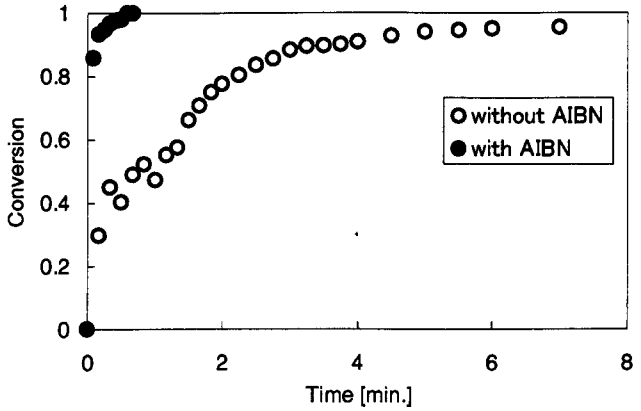


Figure 2. Conversion rate of PA during the copolymerization with *cyclo*-$(MeAs)_5$ without AIBN in chloroform at 25 °C (○) or with AIBN in toluene at 60 °C (●). Mesitylene was employed as a standard material.

AIBN is explained by the difference in the rate of the collapse of the ring structure. The cleavage of the arsenic-arsenic bonds of the cyclooligoarsines was accelerated by a catalytic amount of AIBN, which was proved by the reaction of the cyclooligoarsines with AIBN in the absence of PA. The large contribution of a radical initiator suggests that the copolymer chain propagates via radical species.

In order to examine the growth process of the copolymer chain during the copolymerization in chloroform at 25 °C, the molecular weight change was monitored by GPC analysis. Similarly to the GC analysis, a small amount of the reaction mixture was siphoned, diluted with chloroform, and analyzed by the GPC (Figure 3). As the reaction proceeded, the peak assigned to the poly(vinylene-arsine) gradually shifted to left, suggesting the progressive growth of the polymer chain. The two peaks which appeared in the region of the molecular weight of several hundreds (elution time; 11 - 12 minutes) showed no change in the molecular weight during the copolymerization. The GPC analysis of the spontaneous copolymerization in chloroform at 50 °C was also carried out and exhibited no significant difference of the rate of the chain growth compared to the copolymerization in chloroform at 25 °C. The molecular weight of the copolymer at the peak top (M_p) in the GPC trace (vs. polystyrene standards) is plotted as a function of the conversion rate of PA in Figure 4. The steep increase of the molecular weight of the polymer with the increase of the conversion rate of PA was observed in the range of high conversion. This is a typical feature of step-reaction polymerizations such as polycondensation and polyaddition.

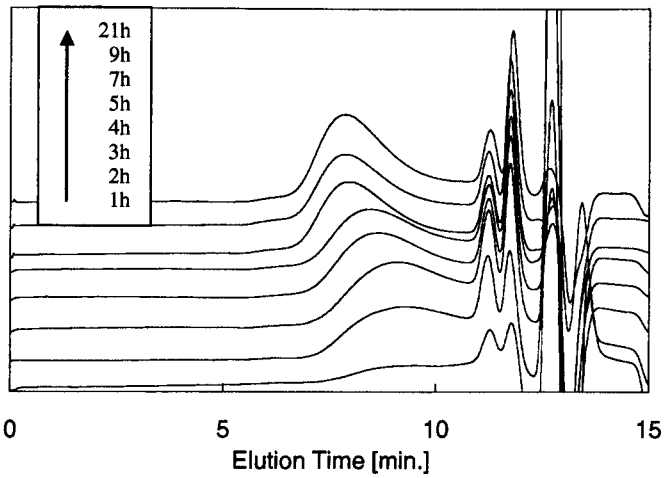


Figure 3. GPC traces of the reaction mixture during the copolymerization of *cyclo*-(MeAs)$_5$ with PA in the absence of AIBN in chloroform at 25 °C.

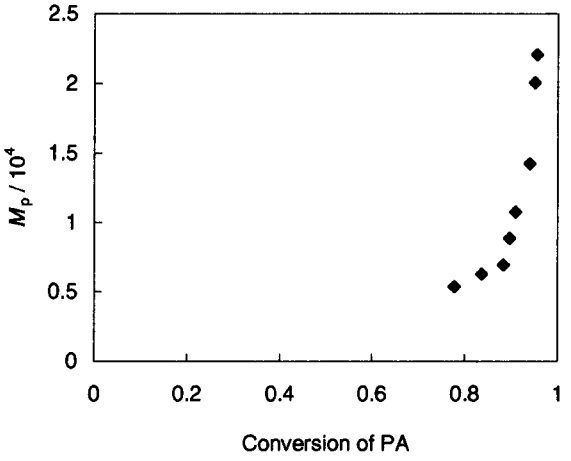


Figure 4. Plot of M_p of poly(vinylene-arsine) in the GPC vs conversion rate of PA during the copolymerization of *cyclo*-(MeAs)$_5$ with PA without AIBN in chloroform at 25 °C.

The copolymerization of *cyclo*-(MeAs)$_5$ with PA using AIBN in chloroform at 50 °C for 2 h also yielded the poly(vinylene-arsine) (M_n = 6 200, M_w/M_n = 1.8), which was also analyzed by GPC (Figure 5). The growth of the polymer chain was completed within 30 minutes, which is consistent with the data of GC analysis (Figure 2).

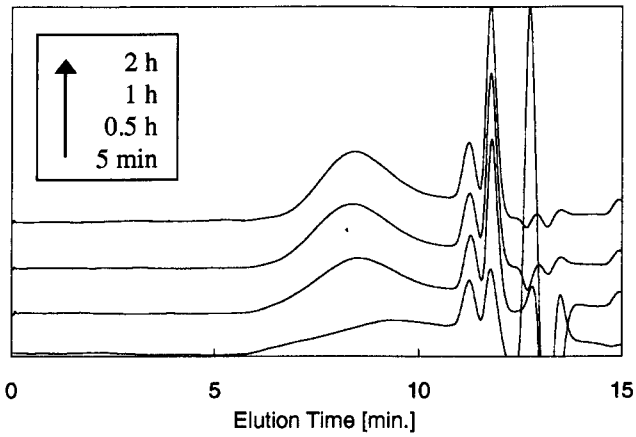


Figure 5. GPC traces of the reaction mixture during the copolymerization of *cyclo*-$(MeAs)_5$ with PA in the presence of AIBN in chloroform at 50 °C.

Summary

Synthesis of novel arsenic-containing polymers, poly(vinylene-arsine)s, has been achieved by ring-collapsed radical alternating copolymerization (*RCRAC*) of arsenic homocycles with PA. In the case of pentamethylcyclopentaarsine, *cyclo*-$(MeAs)_5$, the copolymerization took place without radical initiators or catalysts at room temperature to give 1 : 1 alternating copolymers with the number-average molecular weight of more than ten thousands in moderate yields. In the presence of a radical initiator, the copolymerization was accelerated and completed within 40 minutes. Though further investigations on the mechanism are needed such as ESR analysis, the results of the studies here strongly suggest that the copolymerization proceeds via radical propagating species. In addition, this copolymerization system showed a behavior of step-wise reaction polymerization in the conversion-molecular weight plot and a unique dependency on the monomer feed ratio; the excess MeAs decreases the molecular weight of the copolymer, while the excess PA has no effect on the obtained polymer. The present copolymerization can be regarded as a polyaddition of MeAs having biradical structure with phenylacetylene.

Besides the cyclooligoarsines, a number of cyclic compounds or polymers are known of which ring or chain skeletons are made up of only one inorganic element such as silicon, germanium, phosphorus, antimony, sulfur, and so on.[11] These compounds often cause

homolytic cleavage by stimulation such as light or heat. The present methodology, which involves the homolytic cleavage of element-element bond of inorganic homocycles or homochains and the addition of the produced inorganic radicals to the organic monomers, would be applicable to the preparation of various inorganic polymers containing inorganic elements in the main chain.

Experimental Section

Materials. Unless otherwise noted, all reagents and chemicals were purchased from Wako Pure Chemical Industries, Ltd. Toluene (water < 30 ppm) was bubbled with a stream of nitrogen before use. *n*-Hexane (water < 30 ppm), methanol (water < 50 ppm), and mesitylene were used without further purification. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Phenylacetylene (PA) was purchased from Aldrich and purified by distillation under reduced pressure. Pentamethylcyclopentaarsine (*cyclo*-$(MA)_5$)[12] and hexaphenylcyclohexaarsine (*cyclo*-$(PA)_6$)[13] were synthesized using literature procedures.

Equipment. All reactions and manipulations were carried out under an atmosphere of prepurified nitrogen using Schlenk techniques. ^1H and ^{13}C NMR spectra were obtained using a JEOL JNM-EX270 instrument (270 and 67.5 MHz, respectively) for solutions in $CDCl_3$ and were referenced to $SiMe_4$ (TMS). Gel permeation chromatography (GPC) was carried out on a TOSOH UV-8011 and RI-8000 (Shodex K-803L column) using $CHCl_3$ as an eluent after calibration with standard polystyrene. Gas chromatography (GC) analyses were carried out on a SHIMADZU GC-17A using helium gas as a carrier gas. Thermogravimetric analysis (TGA) was performed on a TG/DTA6200, Seiko Instruments Inc. at the rate of 10 $^\circ C min^{-1}$. Differential scanning calorimetry (DSC) thermograms were obtained with a DSC200, Seiko Instruments Inc., with the heating rate of 10 $^\circ C min^{-1}$ under nitrogen atmosphere. The analysis of the low molecular weight compounds obtained was carried out on a recycling preparative high pressure liquid chromatography (HPLC) (Japan Analytical Industry Co. Ltd., Model 918R) equipped with JAIGEL-1H and 2H columns (GPC) using chloroform as an eluent.

Copolymerization in the Absence of AIBN. A typical experimental procedure was conducted as follows. To a chloroform solution (3.0 mL) of *cyclo*-$(MeAs)_5$ (0.556g, 1.24 mmol), PA (0.631 g, 6.18 mmol) was added all at once at room temperature. The reaction mixture was stirred for 12 h and then poured into *n*-hexane to precipitate a polymeric material. After reprecipitation from toluene into *n*-hexane twice, the resulting precipitate was freeze-dried for 10 h. A bright yellow powder was obtained (0.765 g) in 64 % yield. ^{1}H-NMR (δ, ppm): 0.80 (As-CH_3), 6.21 (*(E)*-C=CH), 6.43 (*(Z)*-C=CH), 6.81 (ArH_o), 7.24 (ArH_m, ArH_p). ^{13}C-NMR (δ, ppm): 10.3 (As-CH_3), 126-129 ($C_{Ar}H_o$, $C_{Ar}H_m$, $C_{Ar}H_p$), 137-140 (C=*C*H), 140.1 (C_{Ar}-C), 155-159 (*C*=CH).

Copolymerization in the Presence of AIBN. A typical experimental procedure was conducted as follows. To a chloroform solution (3.0 mL) of *cyclo*-$(MeAs)_5$ (0.549g, 1.22 mmol), AIBN (0.030 g, 0.018 mmol) and PA (0.623 g, 6.10 mmol) were added at room temperature. The mixture was stirred at 60 °C for 2 h and then poured into *n*-hexane to precipitate the polymeric material. After reprecipitation from toluene into *n*-hexane twice, the resulting precipitate was freeze-dried for 10 h. A bright yellow powder was obtained (0.588 g) in 50 % yield. The ^{1}H and ^{13}C NMR spectra of the resulting polymer were identical with those of the copolymer obtained without AIBN.

Emulsion Polymerization. The reaction mixture of water (10.0ml), *cyclo*-$(MeAs)_5$ (2.45g, 5.44mmol), PA (2.78g, 27.2mmol), sodium lauryl sulfate (0.5g), and potassium peroxodisulfate (0.05g) was stirred vigorously under a nitrogen atmosphere for 8 h at 80 °C. Then the mixture was poured into methanol and the precipitate was washed by methanol. The obtained polymer was purified by reprecipitation into *n*-hexane three times and freeze-dried for 10 h to yield the corresponding poly(vinylene-arsine) as a bright yellow powder (1.42 g, 27% yield). The ^{1}H and ^{13}C NMR spectra of the resulting polymer were identical with those of the copolymer obtained above.

Stability of the Methyl-Substituted Poly(vinylene-arsine). A chloroform solution (10 mL) of the methyl-substituted poly(vinylene-arsine) (0.54 g) was stirred for 24 h at 50 °C. During the stirring, a small amount of the solution was siphoned, diluted with chloroform, and analyzed by GPC, suggesting no decrease of the molecular weight. The ^{1}H NMR spectrum of the polymer recovered after the stirring was identical with that of the starting polymer.

GC Analysis of the Reaction Mixture during the Copolymerization without AIBN. To a chloroform solution (2.0 mL) of PA (0.640 g, 6.26 mmol) and mesitylene (0.50 mL), a chloroform solution (0.50 mL) of *cyclo*-$(MeAs)_5$ (0.563g, 1.25 mmol) was added all at once at room temperature. The moment of the addition was defined as the start time of the copolymerization. During the copolymerization, a small amount of the reaction mixture was siphoned, diluted with chloroform, and analyzed by GC. The consumption rate of PA was calculated from the peak area ratio of PA and mesitylene.

GC Analysis of the Reaction Mixture during the Copolymerization with AIBN. To a toluene solution (1.0 mL) of *cyclo*-$(MeAs)_5$ (0.553 g, 1.23 mmol) and mesitylene (0.50 mL), a toluene solution (1.5 mL) of PA (0.628g, 6.15mmol) and AIBN (0.030 g, 0.018 mmol) was added all at once at 60 °C. The GC analysis was carried out as described above.

GPC Analysis of the Reaction Mixture during the Copolymerization without AIBN. To a chloroform solution (3.0 mL) of *cyclo*-$(MeAs)_5$ (0.563 g, 1.25 mmol) PA (0.639 g, 6.26 mmol) was added and the mixture was stirred at room temperature. The moment of the addition was defined as the start time of the copolymerization. During the copolymerization, a small amount of the reaction mixture was siphoned, diluted with chloroform, and analyzed by GPC.

GPC Analysis of the Reaction Mixture during the Copolymerization with AIBN. To a chloroform solution (1.0 mL) of *cyclo*-$(MeAs)_5$ (0.566 g, 1.26 mmol) a chloroform solution (2.0 mL) of PA (0.643 g, 6.29 mmol) and AIBN (0.030 g, 0.018 mmol) was added at 50 °C. The GPC analysis was carried out as described above.

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Chapter 3

Ring-Collapsed Radical Alternating Copolymerization (*RCRAC*) of Phenyl-Substituted Cyclooligoarsine with Acetylenic Compounds: Substituent Effect and Optical Properties

Abstract: The radical reaction between hexaphenylcyclohexaarsine (**1**) and acetylenic compounds with various substituents (**2a-d**) using a catalytic amount of AIBN provided the corresponding alternating copolymer, poly(vinylene-arsine). The copolymers obtained were soluble in common organic solvents such as THF, chloroform, benzene, and toluene. From gel permeation chromatographic analysis (chloroform, PSt standards), the number-average molecular weights of the copolymers were found to be several thousands. Structural characterization of the copolymers was provided by ^{1}H and ^{13}C NMR spectroscopies. The measurement of the conversion rate of **2a-d** during the copolymerization by using gas chromatography gave an evidence to support the assumption that the formation of vinyl radicals by addition of arsenic radicals to acetylenic compounds was the rate-determining step in this copolymerization system. The copolymer obtained showed fluorescence properties which were influenced by the substituents of the acetylenic compounds.

Introduction

Polymers containing inorganic elements in the main chain structure are of current interest as a result of their unique properties.[1] For example, phosphorus containing polymers have found a variety of important uses including flame retardants[2], ionic conducting materials[3], and easily separable supports for metal catalysts.[4] Recently, conjugated organophosphorus polymers were synthesized and showed interesting features such as significant extension of conjugation along the polymer backbone via the lone pair on P, fluorescent properties, and electron-donating character.[5] On the other hand, the organoarsenic chemistry has a long history that dates back to the synthesis and discovery in 1760 of the first organometallic compound, $Me_2AsAsMe_2$, by L. C. Cadet de Gassicourt.[6] The discovery of the medicinal action of organoarsenicals on syphilis in 1910 led to a rapid expansion of the work on arsenic derivatives. Since an alternative cure was developed in 1940s, less attention has been paid to chemotherapy roles and more to structures, stereochemistry and donor properties of organoarsenic compounds. In the abundant accumulation of the organoarsenic chemistry, however, the incorporation of arsenic into polymer backbones has been limited.[7]

The development of a new polymerization reaction makes it possible to create polymers having a unique structure which is difficult to construct by conventional procedures. As a part of the program in Chujo's laboratory to explore the synthesis and properties of inorganic and organometallic polymers,[5c,8] it is described in Chapter 1 that the ring-collapsed radical alternating copolymerization (*RCRAC*) of arsenic homocycle (**1**) as arsenic atomic biradical equivalent with phenylacetylene (**2a**) yielded the first soluble organoarsenic polymer, poly(vinylene-arsine) (**3a**).[9] This is quite different from conventional radical alternating copolymerizations, which are achieved by donor-acceptor monomer pairs.[10,11] In this chapter, in addition to **2a**, new comonomers such as 4-cyanophenylacetylene (**2b**), 4-methoxyphenylacetylene (**2c**), 1-naphthylacetylene (**2d**), and 1-hexyne (**2e**) were employed and the behaviors of their copolymerizations with hexaphenylcyclohexaarsine (**1**) were investigated to consider the copolymerization mechanism. In addition, here reports interesting optical properties of the copolymers obtained.

Results and Discussion

Synthesis and Characterization of Polymers. Copolymerization of **1** and **2a-d** was carried out in refluxing benzene using 2,2'-azobisisobutyronitrile (AIBN) as a radical initiator (Scheme 1). The copolymers obtained were purified by reprecipitation from benzene to *n*-hexane. The results of the copolymerization are summarized in Table 1. In the case that 1-hexyne (**2e**) was treated with **1** and AIBN in refluxing benzene, no high-molecular-weight material was obtained after stirring for 10 h. The structures of the polymers (**3a-d**) were confirmed by ^{1}H and ^{13}C NMR spectra. The ^{1}H NMR spectrum of **3b** showed broadened peaks around 5.9 – 7.8 ppm which were assigned to aromatic protons and vinyl proton. The signal due to the acetylenic proton of the monomer **2b**[12] completely disappeared, indicating that the ethynyl group of **2b** was converted to vinyl groups in the main chain of copolymer **3b**. To confirm that the cyano group of **2b** has no reactivity toward **1** or AIBN, a mixture of **1** and benzonitrile was treated with AIBN in refluxing benzene. After stirring for 12 h, benzonitrile remained intact according to gas chromatography. Consistently, the ^{13}C NMR spectrum of **3b** showed no peaks corresponding to ethynyl group (around 81 ppm)[12] but the peaks of vinyl group at 136 (-***C***H=C-) and 158 (-CH=***C***-) ppm. The molecular weight measurements were performed by gel permeation chromatography (GPC) in $CHCl_3$ eluent using a calibration curve of polystyrene standards (Table 1). The number-average molecular weight (M_n) of **3b** was estimated to be 8 400, which corresponds to a degree of polymerization of 30, with M_w/M_n = 1.8. All the copolymers (**3a-d**) were soluble in common organic solvents such as THF, $CHCl_3$, benzene, and toluene. These polymers were stable to oxygen and water on exposure to air for several months.

Scheme 1

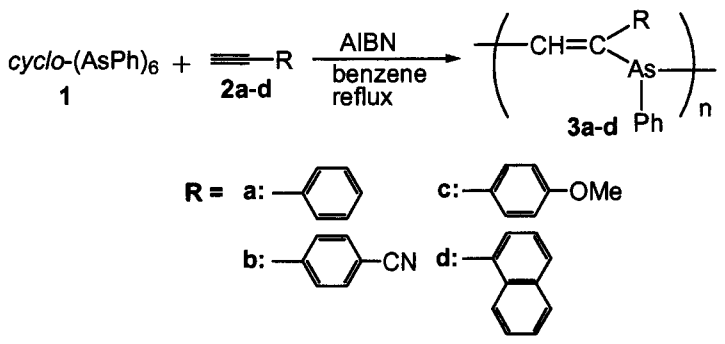


Table 1. Syntheses and Optical Properties of Polymers **3a-e**

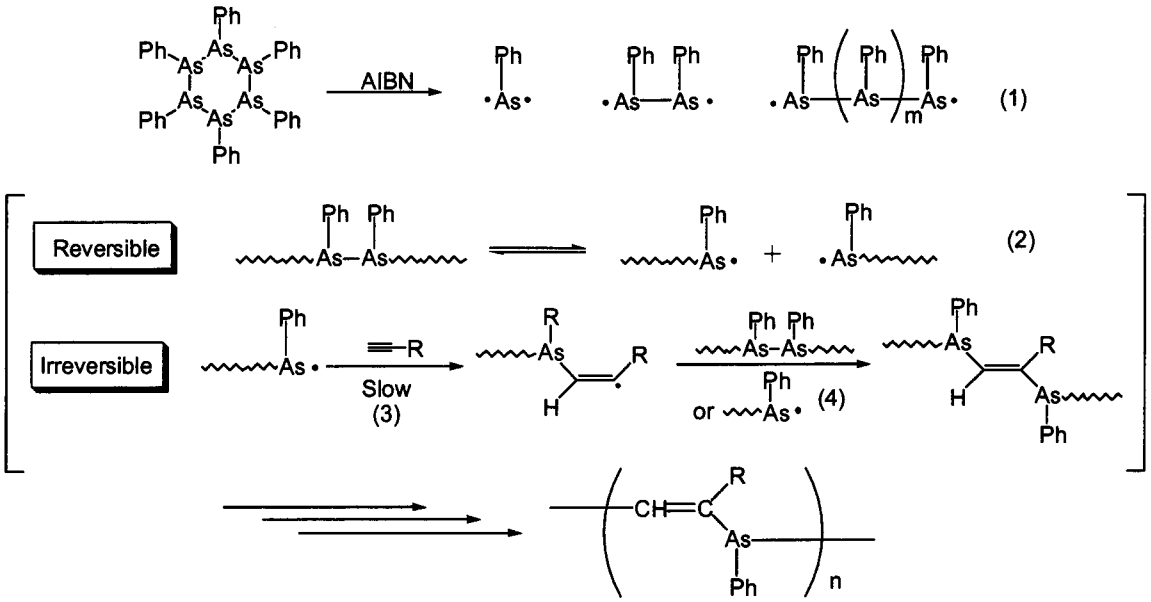
Run	**2**	M_w[a]	M_n[a]	M_w / M_n[a]	Yield (%)[b]	DP[c]	Emission λ_{max} (nm)[d]	Excitation λ_{max} (nm)[d]
1	**2a**	5600	3900	1.4	35	15	437	375
2	**2b**	15100	8400	1.8	29	30	443, 466	394
3	**2c**	5100	3700	1.4	22	13	402	341
4	**2d**	9900	7600	1.3	33	25	350	315
5	**2e**	No Polymer						

[a] GPC ($CHCl_3$). Polystyrene standards. [b] Isolated yields after reprecipitation into *n*-hexane. [c] Degree of polymerization. [d] Recorded in dilute $CHCl_3$ solutions at room temperature.

Discussion of the Copolymerization Mechanism. The following reaction mechanism was proposed for the radical alternating copolymerization as discussed in Chapter 1 (Scheme 2).[9] First, AIBN cleaved arsenic-arsenic bonds of **1** to produce arsenic radicals. Second, the homolysis of the other arsenic-arsenic bonds proceeded spontaneously due to their instability by the destruction of the quite stable six-membered ring structure. In competition with this reaction, an arsenic radical added to an acetylenic compound to give a vinyl radical. Next, a vinyl radical reacted immediately with an arsenic-arsenic bond or with an arsenic radical to form a new carbon-arsenic bond. Although the carbon-arsenic bond formation seems to result in losing a growing radical and no chain growth proceeds anymore, the labile As-As bonds in the product caused homolysis easily to produce a new arsine radical, and the chain growth could restart. In this manner, repeating production of the arsine radical by the As-As bond cleavage and its addition to the acetylenic compound leads to a polymer with a simple main-chain structure, poly(vinylene-arsine). Since the vinyl radicals are more instable and reactive than the arsenic radicals, formation of the vinyl radicals (eq. 3) should be relatively slower than creation of the arsine radical (eq. 2) and of a carbon-arsenic bond (eq. 4). One of the propagating radicals in this copolymerization system is the vinyl radical, which might not cause recombination due to the low concentration. The vinyl radical might not react with the acetylenic compound to produce a new vinyl radical because of its instability, but reacts with an arsenic radical or an arsenic-arsenic bond. The other propagating radical is the arsenic radical which cannot cause disproportionation as

a termination reaction. A recombination of the arsenic radical generates an As-As bond which is easily cleaved under the benzene refluxing condition to reproduce the propagating arsenic radicals.

Scheme 2



Radical reaction of 1-hexyne (**2e**) with **1** provided no high molecular materials (Table 1, Run 5), suggesting that the alkyl-substituted vinyl radical was too unstable to be formed. The aromatic stabilization of the vinyl radical is essential for the copolymerization. It is speculated that the more effectively aromatic stabilization acts on the vinyl radical, the more smoothly the copolymerization progresses. Here is shown the examination of the rates of conversion of monomers **2a-d** during the copolymerization with **1**. The radical copolymerization of **2a-d** with **1** was carried out in the presence of *n*-alkane as a reference material to monitor the amount of consumption of monomers **2a-d** by using gas chromatography (GC). In each experiment, the same concentration of AIBN (0.006 mol/L), **1** (0.060 mol/L), acetylenic compound (0.36 mol/L), and *n*-alkane (0.04 g/L) were used in benzene at 78 °C. The moment of feeding AIBN to the mixture of **1** and acetylenic compounds **2a-d** in refluxing benzene was defined as initiating point (0 min) of the copolymerization. All of the experiments were performed three times, and the average values are presented with error bars in Figure 1. In every copolymerization, the

consumption of acetylenic monomers **2a-d** was induced by addition of AIBN, and almost ceased in 4 h. In the case of using cyano-substituted phenylacetylene **2b**, the polymerization proceeded to reach nearly quantitative conversion. The rate increased in the order **2c** < **2a** < **2d** < **2b**. The copolymerization of **1** with **2b** or **2d** was faster than that with **2a** because the aromatic stabilization of the vinyl radical by 4-cyanophenyl or naphthyl group is stronger than that by phenyl group. The copolymerization of **1** with **2c** was slightly slower than that with **2a**, suggesting that electrostatic effect of the substituent might affect the reaction between arsenic radical and carbon-carbon triple bond. The arsenic radical may prefer to react with electron-accepting monomers rather than electron-donating monomers due to the lone pair on the arsenic atom. Both conjugative and electrostatic effect of 4-cyanophenyl group made the fastest consumption of **2b** during the copolymerization with **1** among the acetylenic monomers employed here. The GC analyses suggest that the less activation energy of the reaction eq. 3 (formation of the vinyl radical) results in the more rapid progress of the total copolymerization. These results are consistent with the speculation and therefore support the mechanism of the copolymerization as proposed above.

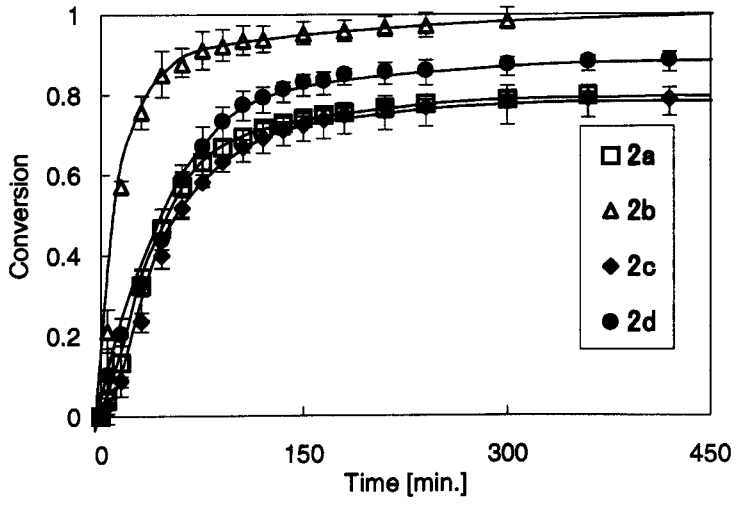


Figure 1. Time-conversion plots of **2a-d** during the copolymerization with **1**.

Optical Properties of the Polymers 3a-d. The electronic structures of the polymers **3a-d** were studied by UV-vis spectroscopy. Figure 2 shows an absorption spectrum of **3b** recorded in chloroform at room temperature. Not only strong absorption in the UV region derived from π–π* transition of the benzene ring, but also small absorption in the visible region was observed. The absorption edge located at around 480 nm. It is assumed that n-π* transition in the main chain brought about the lower energy absorption as seen in poly(phenylene-phosphine)s.[5d]

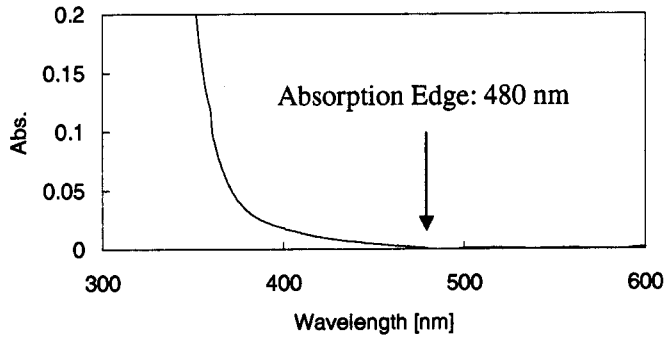


Figure 2. UV-vis absorption spectrum of **2b** in $CHCl_3$ at room temperature.

The polymers **3a-d** showed fluorescent properties. The fluorescence and excitation spectra of a dilute chloroform solution of **3b** measured at room temperature are shown in Figure 3 as a typical representative example. The emission was observed in the visible blue-purple region with a peak at 443 and 466 nm. The emission peak maximum was independent of the concentration of polymer **3b**. In the excitation spectrum of **3b** monitored at 470 nm, the absorption was not observed in the shorter wavelength region but in the longer wavelength region with a peak at 394 nm. This means that the absorption of **3b** in the higher energy region and the absorption in the lower energy region are originated from the different absorbing species; π–π* and n-π* transition. The emission of **3b** results from only the absorption of the latter transition. Table 1 also summarizes emission and excitation spectral data. Each emission peak maximum of **3a-c** was red-shifted in the order **3c** < **3a** < **3b**, which coincides with the order of strength of electron-withdrawing properties of the substituents. This indicates that the donor-acceptor (arsenic atom with a lone pair and vinylene unit with electron-accepting group) repeating units made the band gap narrower and

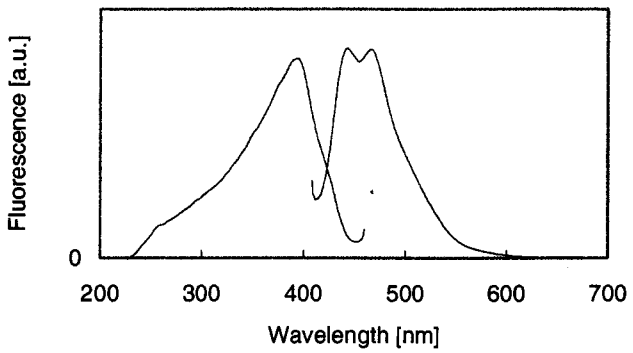
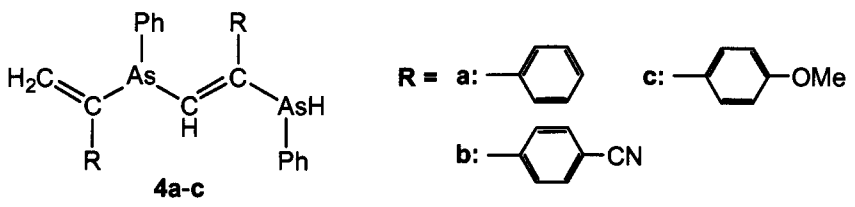


Figure 3. (a) Fluorescence spectrum of **3b** excited at 394 nm. (b) Excitation spectrum of **3b** emitted at 466 nm. Both measurements were carried out in $CHCl_3$ at room temperature.

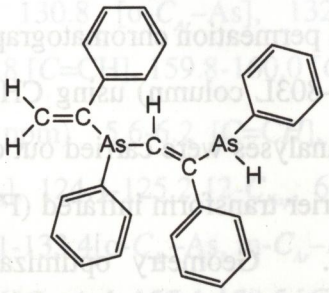
resulted in the lower energy of the emission. The optical properties of poly(vinylene-arsine)s were tuned by changing the substituents of the acetylenic compounds. In the case of **3d**, the naphthyl group itself has a fluorescent property which is stronger than that derived from the n-π* transition in the main chain of the polymer, and therefore the emission peak due to the main chain was hidden. The absorption peaks in the excitation spectra of **3a-d** showed the same order as the emission peaks because of the same reason discussed above.

Calculation of HOMO and LUMO of dimer models (**4a-c**) of **3a-c** (Chart 1) was carried out using the CNDO/S Hamiltonians. The arsenic atom of **4a** bears large electron density of lone pair at HOMO, while no electron density of lone pair is observed at LUMO (Figure 4). LUMO of **4a** shows electron density of π* of styrene unit. These results support the assumption that the lower energy absorption is attributable to n-π* transition in the main chain of the polymer. The HOMO-LUMO band gaps of the dimers increase in the order **5b** < **5a** < **5c**. The cyano groups of **5b** enhance the electron-withdrawing ability of the π-electron system and lower the level of LUMO. The electron-donating methoxy groups of

Chart 1



5c brought about the much higher LUMO level compared to that of **5a** or **5b**. The substituent group of the acetylenic compounds influenced the LUMO levels of the dimers more than HOMO levels. These results are consistent with the emission or excitation spectral data of the polymers **3a-c** (Table 1) where the higher electron-accepting ability leads to the more red-shifted emission or absorption peak.



LUMO HOMO

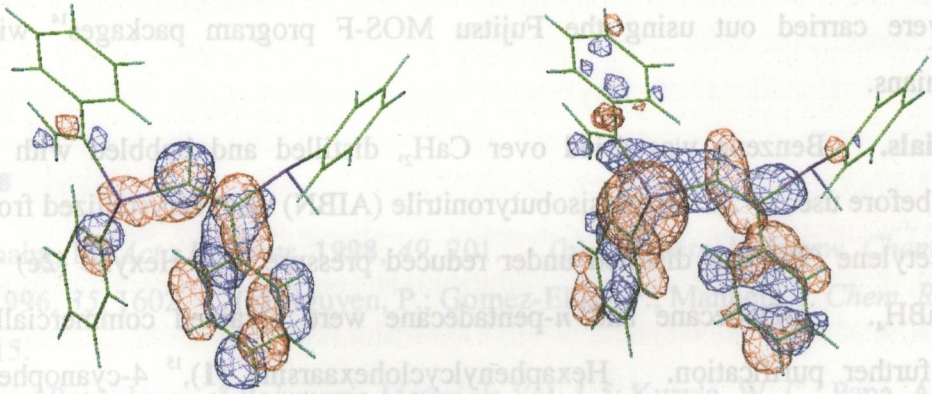


Figure 4. HOMO and LUMO density surface of **4a**.

Summary

The organoarsenic polymers, poly(vinylene-arsine)s, were synthesized by the radical copolymerization of hexaphenylcyclohexaarsine (**1**) with acetylenic compounds with various substituents (**2a-d**). The analyses of the conversion rate of the acetylenic monomers during the copolymerization supported the reaction mechanism proposed in Chapter 1. The poly(vinylene-arsine)s obtained showed the unique optical properties which were tunable by changing the substituent of the acetylenic compound.

Experimental Section

Equipment. ^{1}H and ^{13}C NMR spectra were obtained using a JEOL JNM-EX270 instrument (270 and 67.5 MHz, respectively) for solutions in $CDCl_3$ and were referenced to $SiMe_4$ (TMS). UV-vis spectra were measured on a JASCO V-530 spectrometer, and the samples were analyzed in $CHCl_3$ at room temperature. Fluorescence emission spectra were recorded on a Perkin-Elmer LS50B luminescence spectrometer, and samples were analyzed in $CHCl_3$ at room temperature. Gel permeation chromatography was carried out on a TOSOH UV-8011 and RI-8000 (Shodex K-803L column) using $CHCl_3$ as an eluent after calibration with standard polystyrene. GC analyses were carried out on a SHIMADZU GC-12A using helium gas as a carrier gas. Fourier transform infrared (FT-IR) spectra were obtained on a Perkin Elmer 2000 spectrometer. Geometry optimization was performed using the MOPAC2000 program with the AM1 Hamiltonians.[13] Calculations for HOMO and LUMO levels were carried out using the Fujitsu MOS-F program packages[14] with CNDO/S Hamiltonians.

Materials. Benzene was dried over CaH_2, distilled and bubbled with a stream of nitrogen before use. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Phenylacetylene (**2a**) was distilled under reduced pressure. 1-Hexyne (**2e**) was distilled from $NaBH_4$. *n*-Dodecane and *n*-pentadecane were obtained commercially and used without further purification. Hexaphenylcyclohexaarsine (**1**),[15] 4-cyanophenylacetylene (**2b**),[16,17] 4-methoxyphenylacetylene (**2c**),[16,18] and 1-naphthylacetylene (**2d**)[16,19] were synthesized using literature procedures.

Polymerization. A typical experimental procedure is as follows. Under a nitrogen atmosphere, a benzene solution (0.4 ml) of a catalytic amount of 2,2'-azobisisobutyronitrile (0.005 g, 0.030 mmol) was added to a refluxing benzene solution (4.6 ml) of **2b** (0.229 g, 1.8 mmol) and hexaphenylhexacycloarsine (**1**) (0.273 g, 0.3 mmol). The mixture was stirred for 10 hours, and then poured into *n*-hexane to precipitate the product. After three times reprecipitation from benzene into *n*-hexane, the product was freeze-dried for 10 hours and the corresponding polymer **3b** was obtained as a light-yellow powder. Yield: 0.145 g, 29 %.

3b: ^{1}H-NMR (δ in $CDCl_3$, ppm) 5.8-6.7 [C=C*H*], 6.7-8.0 [Ar-*H*]. ^{13}C-NMR (δ in $CDCl_3$, ppm) 109.8-110.1 [C_{Ar}-CN], 117.4 [*C*N], 126.5 [C_{Ar}-C_{Ar}-C=C], 127.0-129.4 [C_{Ar}-As m-C_{Ar}–As], 130.6-132.5 [p-C_{Ar}–As, C_{Ar}-C_{Ar}-CN] 132.8-140.0 [*C*H=C, o-C_{Ar}–As], 143.9 [C_{Ar}-C=C], 156.0-159.0 [*C*=CH]. IR (cm^{-1}) 2228 [-CN].

3c: ^{1}H-NMR (δ in $CDCl_3$, ppm) 3.4-3.9 [CH_3O], 6.2-6.4 [C=C*H*], 6.4-7.9 [Ar-*H*]. ^{13}C-NMR (δ in $CDCl_3$, ppm) 55.3 [*C*H_3O], 113.2 [C_{Ar}- C_{Ar}-OCH_3], 128.5 [C_{Ar}-C=C, C_{Ar}-C_{Ar}-C=C], 129.1 [*C*H=C], 130.8 [o-C_{Ar}–As], 132.0-133.5 [m-C_{Ar} –As, p-C_{Ar}–As], 140.6-141.1 [C_{Ar}-As], 158.5-158.8 [*C*=CH], 159.8-160.0 [C_{Ar}- OCH_3]. Yield: 22 %.

3d: ^{1}H-NMR (δ in $CDCl_3$, ppm) 5.6-6.2 [C=C*H*], 6.2-8.1 [Ar-*H*]. ^{13}C-NMR (δ in $CDCl_3$, ppm) 123.5-124.1[3-C_{Nap}], 124.1-125.2 [2-C_{Nap}, 6-C_{Nap}, 7-C_{Nap}], 125.6-126.6 [4-C_{Nap}], 126.9-127.3 [5-C_{Nap},8-C_{Nap}], 130.1-133.4[o-C_{Ar}–As, m-C_{Ar}–As, p-C_{Ar}–As], 136.0-138.0 [*C*H=C], 138.2-139.7 [1-C_{Nap}], 139.8-140.6[C_{Ar}-As], 157.4-158.5 [*C*=CH]. Yield: 33 %.

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Chapter 4

Ring-Collapsed Radical Alternating Copolymerization (*RCRAC*) of Organoarsenic Homocycle with Aliphatic Acetylenes

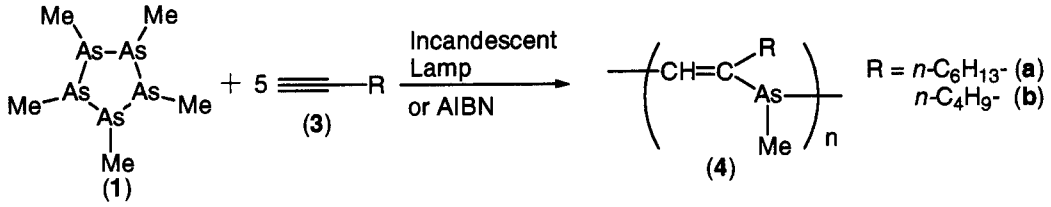
Abstract: Poly(vinylene-arsine)s with no aromatic substituent, $[-CH=CR-AsMe-]_n$, were prepared by a radical alternating copolymerization of acetylenic compounds having an alkyl substituent with an organoarsenic homocycle as an arsenic-atomic biradical equivalent. The radical reaction between 1-octyne and pentamethylcyclopentaarsine, *cyclo*-$(AsMe)_5$, using a catalytic amount of AIBN without solvent (60 °C, 12 h) gave the corresponding poly(vinylene-arsine) (yield; 45 %). The copolymer obtained was soluble in tetrahydrofuran, chloroform, hexane, and so on. The copolymer was characterized by ^1H and ^{13}C NMR spectra. The number-average molecular weight of the copolymer was estimated by gel permeation chromatography (GPC) (chloroform, polystyrene standards) and found to be 6 500. The copolymer showed an emission property attributable to the n–π* transition in the main chain. An irradiation by an incandescent lamp to a mixture of 1-octyne and *cyclo*-$(AsMe)_5$ also produced the poly(vinylene-arsine). The conversion rate of 1-octyne during the copolymerization using AIBN was measured by gas chromatography (GC) analysis and found to be much slower than that of phenylacetylene. A radical terpolymerization of *cyclo*-$(AsMe)_5$ with 1-octyne and styrene was carried out to yield the terpolymer.

Introduction

Cyclooligoarsines[1] are monocyclic compounds with rings built exclusively of arsenic atoms, which are attractive owing to the extreme adaptability of arsenic as a bridging element in metal clusters and the unique coordinating modes in transition metal complexes. There are two typical cyclooligoarsines, pentamethylcyclopentaarsine (**1**)[2] and hexaphenylcyclohexaarsine (**2**),[3] which can be prepared easily by the reduction of the corresponding arsonic acid or its salt with hypophosphorus acid. In the last few decades, a large number of studies have been made on the structural chemistry of their transition-metal complexes.[4] However, the reports on the reaction of cyclooligoarsines with organic compounds are still rare.[1,5]

Chapter 1 describes the ring-collapsed radical alternating copolymerization (*RCRAC*) of organoarsenic homocycles with phenylacetylene (PA), which was induced by a radical initiator or light, to produce the organoarsenic polymer, poly(vinylene-arsine)s [-CH=CPh-AsR-]$_n$.[6] This is the first example of the use of an inorganic ring as a monomer for a radical copolymerization and of the soluble polymer having arsenic atoms in the main chain. This chapter describes the radical copolymerization of cyclooligoarsine with alkyl-substituted acetylenic compounds (Scheme 1). One of the reasons for interests in employing alkynes with an alkyl group as a comonomer is that a substituent group of acetylenic compounds influences the reactivity in analogy with the conventional radical polymerization of vinyl monomers as described in Chapter 3. Here also describes here optical properties of the copolymers obtained.

Scheme 1



Results and Discussion

Polymer Synthesis and Structural Characterization. It is shown in Chapter 1 that the radical copolymerization of pentamethylcyclopentaarsine (**1**) or hexaphenylcyclohexaarsine (**2**) with phenylacetylene (PA) in benzene at 78 °C using a catalytic amount of 2,2'-azobisisobutyronitrile (AIBN) as a radical initiator gave the corresponding poly(vinylene-arsine). The copolymerization of **1** with PA was also achieved by an irradiation of the mixture in benzene with an incandescent lamp or a xenon lamp, while **2** showed no reaction with PA by the irradiation. For the work in this chapter, the radical copolymerization of **1** or **2** was examined with aliphatic alkynes such as 1-octyne (**3a**), 1-hexyne (**3b**), or 3-hexyne (**3c**) with AIBN or an incandescent lamp.

In the first place, a radical reaction between **1** and **3a** was carried out with a catalytic amount of AIBN ($[AIBN]_0$ / $[\mathbf{3a}]_0$ = 0.030) without solvent (Scheme 1). The yellow color due to **1** faded gradually and disappeared almost completely after 10 h. Precipitation from toluene to acetone yielded the corresponding poly(vinylene-arsine) (**4a**) as a bright yellow gum (yield; 45 %), which was soluble in common organic solvents such as toluene, chloroform, tetrahydrofuran, and *n*-hexane. The trace on gel permeation chromatogram (chloroform as an eluent) of **4a** showed a single peak. The number-average molecular weight of **4a** determined by gel permeation chromatography (polystyrene standards) was estimated to be 6 500 with a polydispersity index of 1.2 (Table 1, Run 1). The relatively narrow molecular weight distribution was due to the removal of low molecular weight material by the reprecipitation. ^{1}H NMR and ^{13}C NMR were employed to support the

Table 1. Results of Copolymerization

Run	R	Solvent	Initiator	Temperature (°C)	M_n[a]	M_w/M_n[a]	Yield (%)[b]
1	*n*-C_6H_{13}-	None	AIBN	60	6 500	1.2	45
2	*n*-C_6H_{13}-	Toluene	AIBN	60	-	-	0
3	*n*-C_6H_{13}-	None	*hν*[c]	r. t.	5 700	1.3	56
4	*n*-C_6H_{13}-	Toluene	*hν*[c]	r. t.	3 800	1.2	11
5	*n*-C_4H_9-	None	AIBN	60	5 400	1.2	65

[a] Estimated by GPC analysis in chloroform on the basis of polystyrene calibration. [b] Isolated yield after reprecipitation from toluene to acetone. [c] Incandescent lamp (100W).

structure of **4a**. In Figure 1 is shown the ^{1}H NMR spectrum of **4a**, which exhibits two peaks in 6.0-6.3 ppm assigned to vinyl proton of *cis*- and *trans*-isomers. The integral ratio of the two peaks reveals that **4a** contains approximately equal amount of *cis*-form to that of *trans*-form. From the peak area ratio of the vinyl proton and the allyl proton, the copolymer composition, methylarsine unit (AsMe) / 1-octyne unit (CH=C-*n*-C_6H_{13}), is found to be 1.0. The ^{13}C NMR spectrum (Figure 2) of **4a** shows the peaks at 157-161 ppm and 133-137 ppm attributable to the vinyl carbons. Each area has two peaks derived from the *cis*- and *trans*-isomers. Only one sharp resonance for AsCH_3 is observed at 9.4 ppm in Figure 2, suggesting that the copolymerization proceeded highly alternatingly to produce the polymer with the main-chain structure of vinylene-arsine, -C=C-As-.

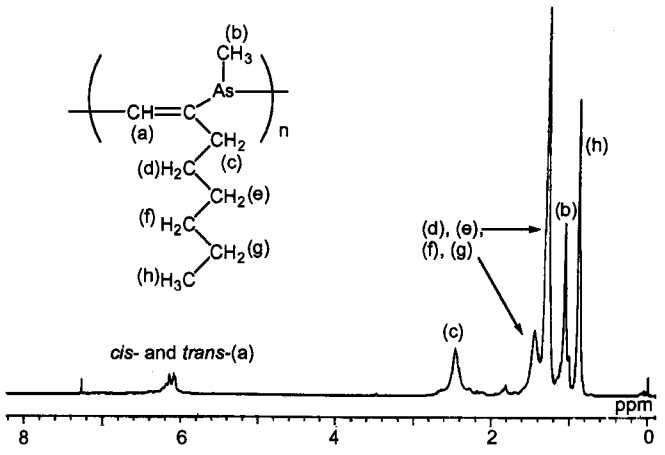


Figure 1. ^{1}H NMR spectrum of **4a** in $CDCl_3$.

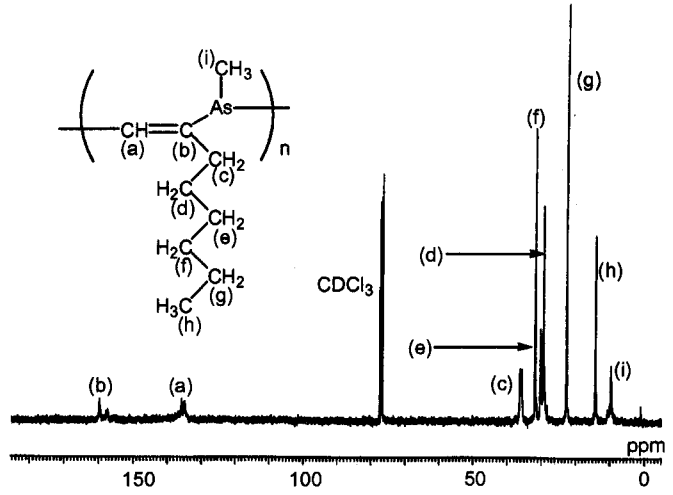


Figure 2. ^{13}C NMR spectrum of **4a** in $CDCl_3$.

The copolymerization was also attempted by stirring a mixture of **1** and **3a** with irradiation by an incandescent lamp for 12 h. A copolymer with the identical structure to **4a** was obtained (yield 56 %, Table 1, Run 3). The use of toluene solution of **1a** and **2** for the copolymerization with AIBN or an incandescent lamp resulted in no polymeric material or the corresponding poly(vinylene-arsine) with lower molecular weight in lower yield (Table 1, Run 2 and 4). The copolymerization of **1** with **3a** without AIBN at room temperature or 60 °C gave no polymeric material while phenylacetylene (PA) copolymerized with **1** without any catalysts at room temperature to form the corresponding poly(vinylene-arsine) as described in Chapter 2.

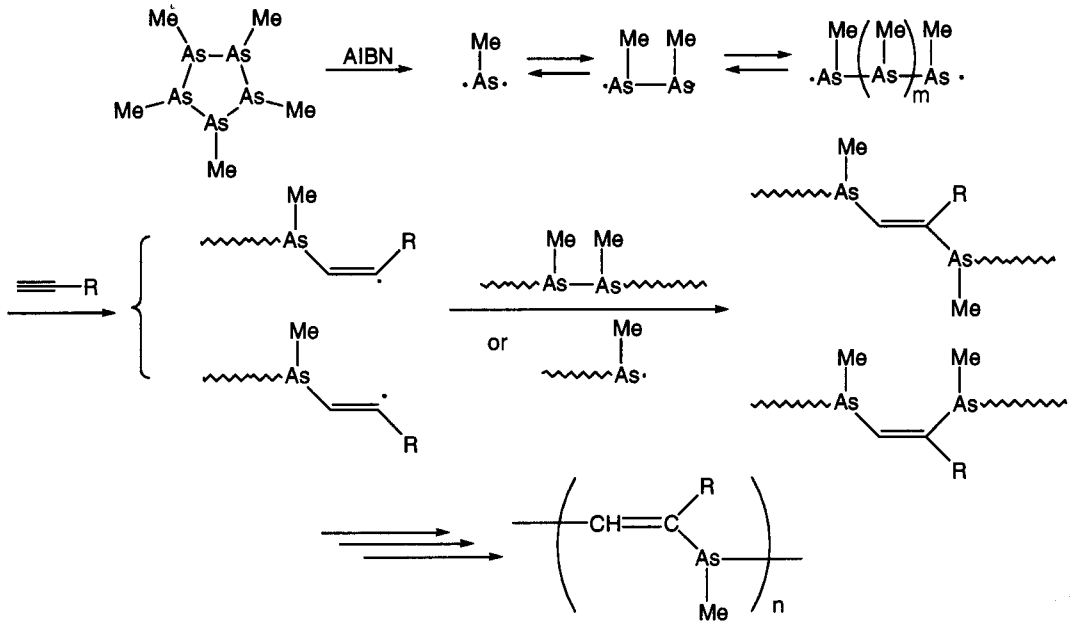
While the radical copolymerization of **1** with 1-hexyne (**3b**) using a catalytic amount of AIBN at 60 °C led to the corresponding poly(vinylene-arsine) with *n*-butyl side chain (Table 1, Run 5), the stirring 3-hexyne (**3c**) with **1** in the presence of either AIBN or an incandescent lamp yielded no corresponding copolymers but yielded purple-black precipitate which was insoluble in any solvents and fuming in the air. Though this troublesome precipitate has not been well characterized yet, it must be linear poly(methylarsine) which stacked each other to form a ladder structure[7] and contained no 3-hexyne unit. Terminal acetylenic group is fatal for aliphatic alkynes to react with methylarsine in this copolymerization system.

Treatment of **2** with **3a** in the presence of AIBN without solvent at 60 °C caused no reaction, because **2** is pale yellow powder which is insoluble in **3a** or toluene. The other cyclooligoarsine **1** is yellow liquid and miscible with **3a** and common organic solvents such as toluene, tetrahydrofuran, and chloroform. When **2** was stirred with **3a** and AIBN in toluene at 60 °C, the heterogeneous mixture became transparent in 30 minutes. However, no polymer was obtained. It can be presumed that the ring structure of **2** was collapsed and then open-chain oligoarsine with terminal arsenic radicals was formed in the same manner as the reaction of **2** with AIBN without **3a**.[6] The open-chain oligoarsine with phenyl substitution could not react with **3a** due to the law reactivity of **3a** compared to that of PA. Conjugative substitutions of ethynyl group increase the reactivity of the acetylenic compounds toward the arsenic radical.

Mechanism of the Copolymerization. The mechanism of the radical copolymerization of **1** with aliphatic acetylenes should be the same as that of the copolymerization of **1** with PA

as discussed in the previous chapters (Scheme 2). First, radical species from AIBN promoted the cleavage of arsenic-arsenic bonds of **1** and the production of the arsenic radicals. These radicals reacted with the ethynyl groups of **3a** to produce vinyl radicals with *cis* and *trans* isomers. The vinyl radicals attacked the arsenic-arsenic bonds or arsenic radicals to form carbon-arsenic bonds. Thus, the cleavage of diarsenic linkages and the formation of the carbon-arsenic bonds were repeated to yield the alternating copolymer, poly(vinylene-arsine).

Scheme 2



The arsenic-arsenic bonds of **1** were cleaved spontaneously even in a light-shielding state at 0 °C to slowly produce the poly(methylarsine) with the ladder structure as purple-black precipitates. When **1** was treated with AIBN at 60 °C or irradiated with an incandescent lamp the formation of the precipitates was accelerated, suggesting that AIBN or *hv* promoted the collapse of the ring structure of **1**. In the case of the copolymerization of **1** with **3a** using AIBN, a plenty of arsenic radicals that arose from the promoted decomposition of **1** had the opportunity for reacting with ethynyl group of **3a**. Once the carbon-arsenic bond was formed, the bond was stable under the condition of the copolymerization (60 °C). In comparison with this case, much less amount of the arsenic radials was present while stirring

the mixture of **1** and **3a** without AIBN. Thus, the reaction of the methylarsine with **3a** was so slow that no polymeric materials were obtained after the reaction for 12 h.

Consumption Rate of Acetylene Monomer during the Copolymerization with 1 Using AIBN. Figure 3 plots the evolution of conversion of **3a** as a function of polymerization time with **1** at 60 °C in the presence of a catalytic amount of AIBN and a comparable amount of *n*-nonane as a reference material. Figure 3 also shows the plots of PA conversion vs reaction time during the copolymerization with **1** using AIBN in toluene at 60 °C. In the latter case, mesitylene was employed as a reference material. In the former case, the consumption of **3a** reached almost 80 % in 4 h, and then the slow and continuous decrease of **3a** which lasted four more hours was observed. In the latter case, 100 % conversion of PA was attained in 40 minutes. Though the copolymerization of PA with **1** was conducted in toluene and that of **3a** was carried out without solvent, PA consumed much faster than **3a**. The higher reactivity of the ethynyl group of PA is attributable to the aromatic stabilization to the produced vinyl radicals. Since the vinyl radicals did not react with **3a** but reacted with arsenic-arsenic bonds and arsenic radicals, the highly reactive vinyl radicals from **3a** did not accelerate the consumption of **3a**. These observations suggest that the formation of the vinyl radical is the rate-determining step of the copolymerization system when the amount of AIBN used was constant.

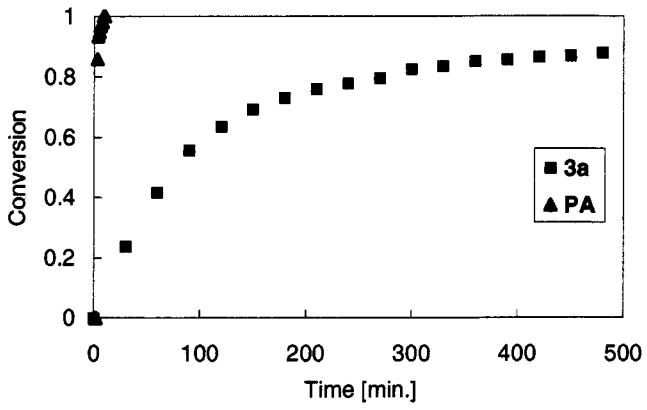
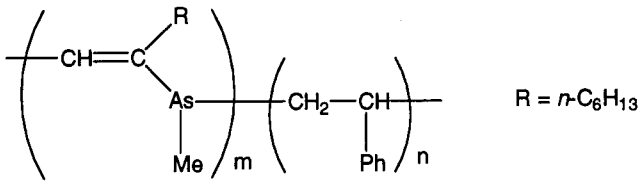


Figure 3. Time-conversion plot of **3a** during the copolymerization with **1** using AIBN with *n*-nonane at 60 °C (■) and of phenylacetylene during the copolymerization with **1** using AIBN in toluene with mesitylene at 60 °C (▲).

Terpolymerization of 1, 3a and Styrene. The terpolymerization of **1**, **3a** and styrene (St) was carried out in the presence of a catalytic amount of AIBN without solvent in the feed ratio, **1** : **3a** : St = 1 : 5 : 5. After the reprecipitation into acetone, a polymeric material was obtained as a colorless gum (yield 12 %). The polymer showed a single peak on its GPC trace. The molecular weight measurement of the obtained polymer was performed by GPC with polystyrene standards. The number-average molecular weight was 6 300 with the molecular weight distribution (M_w/M_n) of 1.8. The ^{1}H NMR and ^{13}C NMR spectra of the polymer showed the several peaks assigned to polystyrene unit other than the peaks for the poly(vinylene-arsine) unit. These observations indicate that the polymeric material obtained was a terpolymer with two kinds of block segments, the poly(vinylene-arsine) and polystyrene, in the backbone structure (Chart 1). The integral ratio of the peaks in the ^{1}H NMR spectrum revealed the composition of the two blocks, m : n = 1 : 0.52. The content of St unit is smaller than the monomer feed ratio of St.

Chart 1



Optical Properties of 4a. The electronic structure of the polymer **4a** was investigated by UV-vis spectroscopy, which was recorded in chloroform at room temperature. Not only strong absorption in the UV region derived from π–π^* transition of C=C, but also small absorption in the visible region attributable to a delocalized n–π^* transition in the backbone[8] was observed. The lower energy absorption edge was located at 500 nm.

The polymer **4a** showed fluorescent properties. The fluorescence and excitation spectra of a dilute chloroform solution of **4a** measured at room temperature are shown in Figure 4. The emission was observed in the visible blue-violet region with a peak at 450 nm by an irradiation at 350 nm. In the excitation spectrum of **4a** monitored at 450 nm, the absorption peak was observed only in the region where the wavelength was more than 310 nm. This

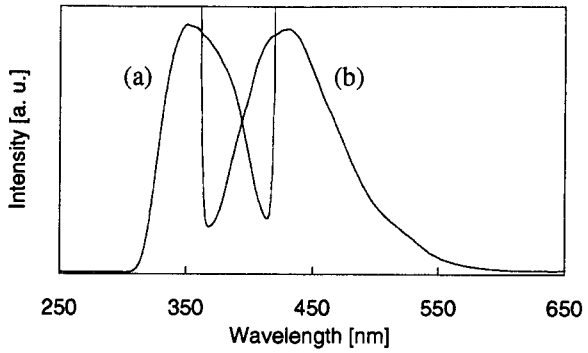


Figure 4. Emission (a) (excited at 350 nm) and excitation (b) (emitted at 430 nm) spectra of **4a** recorded in chloroform at room temperature.

means that the absorption of **4a** in the <310 nm region and the absorption in the >310 nm region are originated from different absorbing species. The emission of **4a** results from only the absorption of the n–π* transition. Both of the emission and excitation peaks of **4a** were blue-shifted in comparison with those of the polymer which was synthesized by the copolymerization of **1** with PA. The substituent groups of the acetylenes affected the electronic structure of the main chain of poly(vinylene-arsine)s.

Summary

The ring-collapsed radical alternating copolymerization (*RCRAC*) of the methyl-substituted organoarsenic homocycle **1** with aliphatic acetylenes in the presence of AIBN or an incandescent lamp irradiation has been achieved to produce the poly(vinylene-arsine)s with no aromatic substitution, while **2** did not copolymerize with aliphatic acetylenes. The progress of the copolymerization of **1** with aliphatic acetylenes was much slower than that with PA due to the lack of the conjugative substitution to the ethynyl group. During the copolymerization with AIBN, the collapse of the arsenic rings and the production of arsenic radicals were much faster than the formation of the vinyl radicals from acetylenes. The copolymer obtained showed emission properties attributable to n–π* transition in the main chain, and the energy band gap was influenced by the substitution.

Experimental Section

Materials. Unless otherwise noted, all reagents and chemicals were purchased from Wako Pure Chemical Industries, Ltd. Dehydrated toluene (water < 30 ppm) was bubbled with a stream of nitrogen before use. Dehydrated acetone (water < 50 ppm), mesitylene, and *n*-nonane were used without further purification. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from methanol. 1-Octyne (**3a**), 1-hexyne (**3b**), and 3-hexyne (**3c**) were distilled from $NaBH_4$. Styrene (St) was distilled under reduced pressure before use. PA was purchased from Aldrich and purified by distillation under reduced pressure. **1**[2] and **2**[3] were synthesized using literature procedures.

Instruments. ^1H and ^{13}C NMR spectra were obtained using a JEOL JNM-EX270 instrument (270 and 67.5 MHz, respectively) for solutions in $CDCl_3$ and were referenced to $SiMe_4$ (TMS). UV-vis spectra were measured on a JASCO V-530 spectrometer, and the samples were analyzed in $CHCl_3$ at room temperature. Fluorescence emission spectra were recorded on a Perkin-Elmer LS50B luminescence spectrometer, and the samples were analyzed in $CHCl_3$ at room temperature. Gel permeation chromatography was carried out on a TOSOH UV-8011 and RI-8000 (Shodex K-803L column) using $CHCl_3$ as an eluent after calibration with standard polystyrene. GC analyses were carried out on a SHIMADZU GC-17A using helium gas as a carrier gas.

Polymerization. Copolymerization of 1 with 3a with AIBN (Run 1). Under a nitrogen atmosphere, a mixture of **1** (0.562 g, 1.25 mmol), **2a** (0.689 g, 6.25 mmol), and AIBN (0.030 g, 0.18 mmol) was stirred at 60 °C for 12 h. After the reaction, the light yellow viscous liquid obtained was dissolved in toluene and the polymer was precipitated with acetone, separated by centrifugation and decantation, and dried in vacuo. A light yellow gum was obtained (0.563 g, 45 %). ^1H NMR (δ, ppm): 6.14, 6.05 (1H, *cis*- and *trans*-C*H*=C), 2.46 (2H, CH=C-CH_2), 1.2-1.6 (8H, -CH_2-), 1.05 (3H, As-CH_3), 0.87 (3H, CH_2-CH_3). ^{13}C NMR (δ, ppm): 159.7, 157.8 (*cis*- and *trans*-CH=*C*), 135.7, 134.9 (*cis*- and *trans*-*C*H=C), 35.9 (C-*C*H_2), 31.5 (C-CH_2-CH_2-CH_2-CH_2-), 30.1 (C-CH_2-CH_2-CH_2-), 28.7 (C-CH_2-CH_2-), 22.7 (-CH_2-CH_2-CH_3), 14.1 (-CH_2-CH_3), 9.4 (As-CH_3).

Copolymerization of 1 and 3a with an Irradiation by Incandescent Lamp (Run 3).

Under a nitrogen atmosphere, a mixture of **1** (0.544 g, 1.21 mmol) and **2a** (0.666 g, 6.05 mmol) was stirred being irradiated by an incandescent lamp (100 W) for 12 h. After the same procedure as above, the copolymer with the same structure as above was obtained (0.640 g, 56 %).

Copolymerization of 1 and 3a in Toluene with an Irradiation by Incandescent Lamp (Run 4). Under a nitrogen atmosphere, a reaction mixture of **1** (0.534 g, 1.19 mmol) and **3a** (0.654 g, 5.94 mmol) in toluene (2.0 mL) was stirred being irradiated by an incandescent lamp (100 W). After ca 36 h, the mixture was decolorized almost completely. The same procedure as above yielded the copolymer (0.130 g, 11 %).

Copolymerization of 1 and 3b with AIBN (Run 5). Under a nitrogen atmosphere, a mixture of **1** (2.50 g, 5.56 mmol) and **3b** (2.29 g, 27.8 mmol) was stirred being irradiated by an incandescent lamp (100 W) for 12 h. After the same procedure as above, a light yellow gum was obtained (3.09 g, 65 %). ^{1}H NMR (δ, ppm): 6.17, 6.11 (1H, *cis*- and *trans*-C*H*=C), 2.48 (2H, CH=C-CH_2), 1.2-1.6 (4H, -CH_2-), 1.06 (3H, As-CH_3), 0.90 (3H, CH_2-CH_3).

Measurement of the Consumption Rate of 3a during the Copolymerization with 1 with AIBN. In the presence of 0.30 mL of *n*-nonane, the copolymerization of **3a** with **1** using AIBN was carried out in the same manner as Run 1. In the course of the copolymerization, the amount of **3a** relative to that of *n*-nonane was monitored in every 30 minutes by using gas chromatography after a small quantity of the reaction mixture was siphoned and dissolved in toluene.

Measurement of the Consumption Rate of PA during the Copolymerization with 1 with AIBN. Under a nitrogen atmosphere, a mixture of **1** (0.553 g, 1.23 mmol), PA (0.628 g, 6.15 mmol), AIBN (0.030 g, 0.18 mmol), and mesitylene (0.50 mL) in toluene (3 mL) was stirred. In the course of the copolymerization, the amount of PA relative to that of mesitylene was monitored in every 5 minutes by using gas chromatography.

Terpolymerization of 1, 3b and St with AIBN. Under a nitrogen atmosphere, a mixture of **1** (0.560 g, 1.25 mmol), **3b** (0.686 g, 6.23 mmol), St (0.648 g, 6.23 mmol), and AIBN (0.030 g, 0.18 mmol) was stirred at 60 °C for 12 h. After the reaction, the colorless viscous liquid obtained was dissolved in toluene and the polymer was precipitated with acetone, separated by centrifugation and decantation, and dried in vacuo. A colorless gum

was obtained (0.232 g, 12 %). ^{1}H NMR (δ, ppm): 6.15, 6.10 (*cis*- and *trans*-C*H*=C), 2.46 (CH=C-CH_2), 0.7–1.7 (the other alkyl protons). ^{13}C NMR (δ, ppm): 159.8, 157.9 (*cis*- and *trans*-CH=*C*), 145.1 (C_{Ar}-C), 135.7, 134.9 (*cis*- and *trans*-*C*H=C), 126-128 ($C_{Ar}H_m$, $C_{Ar}H_p$), 125.8 ($C_{Ar}H_o$), 42-46 (*C*H_2-CH), 40.5 (CH_2-*C*H), 36.1 (C-*C*H_2), 31.5 (C-CH_2-CH_2-CH_2-CH_2-), 30.3 (C-CH_2-CH_2-CH_2-), 29.3 (C-CH_2-CH_2-), 22.7 (-CH_2-CH_2-CH_3), 14.1 (-CH_2-CH_3), 9.7 (As-CH_3).

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Chapter 5

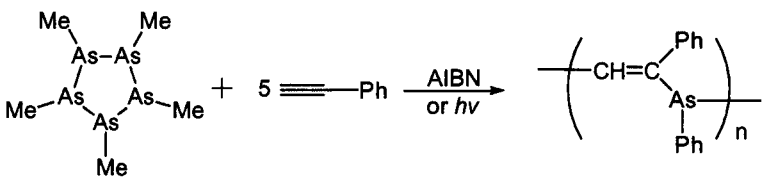
Radical Terpolymerization of Organoarsenic Homocycle, Phenylacetylene, and Vinyl or Butadienyl Monomers

Abstract: The free radical terpolymerization of pentamethylcyclopentaarsine (*cyclo*-$(MA)_5$), phenylacetylene (PA), and various vinyl monomers in toluene is described. The terpolymerization of *cyclo*-$(MA)_5$, PA, and styrene (St) in the molar ratio 1 : 5 : 5 with a catalytic amount of AIBN at 60 °C for 8 h provided a polymer in 38 % yield after reprecipitation. The terpolymer was soluble in common organic solvents such as tetrahydrofuran, chloroform, benzene, and toluene. In the GPC analysis (chloroform, PSt standards), the terpolymer showed a single peak and the number-average molecular weight was estimated to be 10 200. The structure of the terpolymer obtained was compared with those of poly(vinylene-arsine) and polystyrene by use of ^{1}H NMR and ^{13}C NMR and found to have two block units, [poly(MA-*alt*-PA)-poly(St)]. The integral ratio of the peak area in the ^{1}H NMR spectrum revealed the terpolymer composition, MA (methylarsine, MeAs) : PA : St = 1 : 0.99 : 0.56. The terpolymer showed fluorescence property attributable to the n-π^* transition in the poly(MA-*alt*-PA) block. The terpolymerization of *cyclo*-$(MA)_5$, PA, and St in various feed ratios was carried out in the presence of AIBN to yield the terpolymers which possessed poly(MA-*alt*-PA) and poly(St) blocks with various compositions. The terpolymer with the higher content of St unit exhibited the more blue-shifted emission peak. The radical terpolymerization of methyl methacrylate (MMA) with *cyclo*-$(MA)_5$ and PA also yielded the corresponding terpolymer with poly(MA-*alt*-PA) unit and poly(MMA) unit, while the terpolymerization employing vinyl acetate (VA) as a vinyl monomer produced poly(vinylene-arsine) with no VA segment. The radical reaction of 2,3-dimethyl-1,3-butadiene (DB) with *cyclo*-$(MA)_5$ and PA formed a different type of terpolymer which had alternating sequences of MA and PA or DB, e.g., $[(MA\text{-}PA)\text{-}(MA\text{-}DB)]_n$.

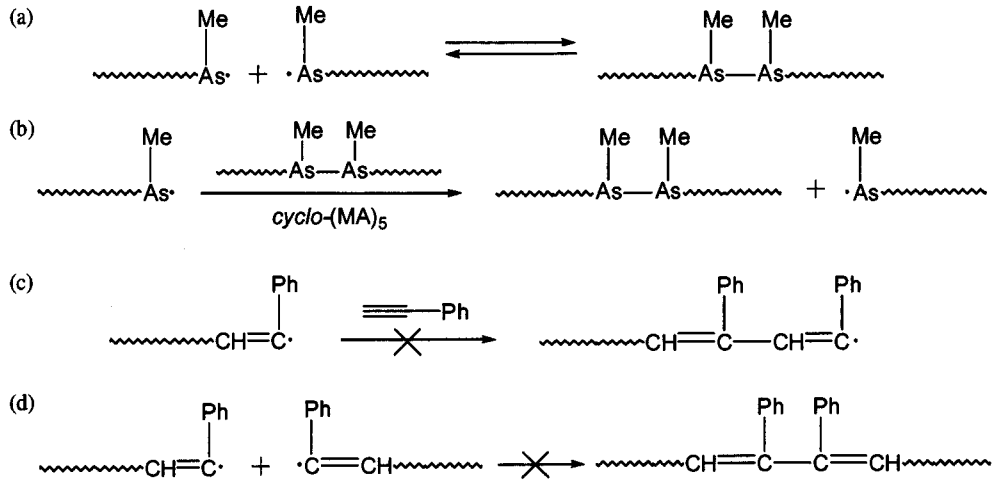
Introduction

For the synthesis of an alternating copolymer of two monomers, M_1 and M_2, one of the most precise controls of the propagating reaction is required in which only the cross-reactions ($M_1 \rightarrow M_2$ and $M_2 \rightarrow M_1$) are repeated alternatingly a number of times with no homo-reactions ($M_1 \rightarrow M_1$ and $M_2 \rightarrow M_2$). Chapter 1 described the synthesis of the novel organoarsenic polymer, poly(vinylene-arsine), by the ring-collapsed radical alternating copolymerization (*RCRAC*) of cyclooligoarsines, of which rings are built exclusively of arsenic atoms, with phenylacetylene (Scheme 1).[1] The poly(vinylene-arsine) is the first example of a soluble polymer containing arsenic atoms in the backbone with well-defined structure. In this system, the radical alternating copolymerization was accomplished by a unique mechanism which is different from mechanisms reported previously.[2] One of the propagating radicals here is an arsenic radical which arises from the cleavage of the arsenic-arsenic bond of the arsenic homocycle. When the arsenic radical reacts with another arsenic radical the diarsenic linkage is formed, which is unstable and tends to cause the homolysis reproducing the propagating arsenic radicals (Scheme 2a). Thus, the recombination reaction of the arsenic radicals is not a termination reaction of this copolymerization. The attack of the arsenic radical to the arsenic homocycle or the arsenic-arsenic bond also leads the labile As-As bond and a new propagating arsenic radical (Scheme 2b). In addition, the arsenic radicals never bring about disproportionation reaction. The other monomer, phenylacetylene, has a low homopolymerizability. The propagating ethynyl radical rarely attacks phenylacetylene (Scheme 2c). The recombination reaction of the ethynyl radicals seldom occurs, which is explained by the low concentration of the ethynyl radicals due to the high reactivity (Scheme 2d). Thus, the cross-reactions are repeated with the cleavage of As-As bonds to produce the alternating copolymer, poly(vinylene-arsine).

Scheme 1



Scheme 2



This chapter provides various vinyl monomers coexistent for this unique radical copolymerization system of the arsenic homocycle and phenylacetylene. Recently, free radical terpolymerizations of electron-rich monomers with electron-accepting monomers, which result in terpolymers with alternating sequences of the donor and acceptor monomers, are studied intensively in view of the scientific position.[3] Here describes the radical terpolymerization of the arsenic homocycle, phenylacetylene, and a vinyl monomer in the presence of a radical initiator (Scheme 3). The obtained polymer was a terpolymer which possessed two block segments of poly(vinylene-arsine) and the vinyl polymer (Chart 1). This is the first example of a terpolymer with the structure of [poly(M_1-*alt*-M_2)-poly(M_3)] synthesized by a simple radical terpolymerization of M_1, M_2, and M_3. The relationship of the terpolymer composition and optical properties is also a subject of this study. In addition, the radical terpolymerization using 2,3-dimethyl-1,3-butadiene instead of vinyl monomers was investigated.

Scheme 3

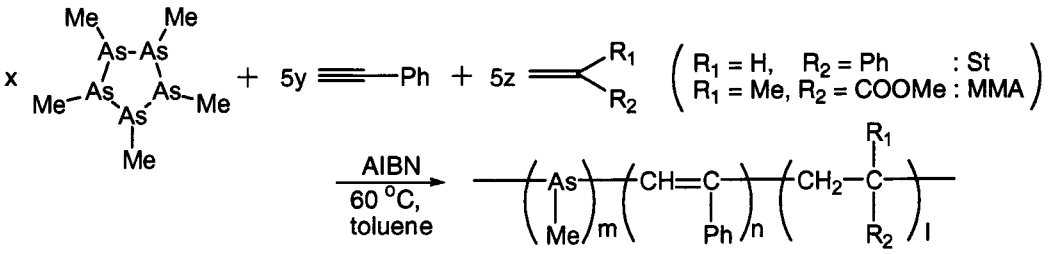
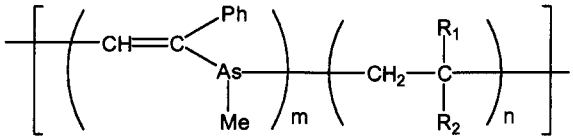


Chart 1



Results and Discussion

Terpolymerization of *cyclo*-$(MA)_5$, PA, and St. The radical terpolymerization of *cyclo*-$(MA)_5$, PA, and St (Scheme 3, R_1 = H, R_2 = Ph) in the feed ratio 1 : 5 : 5 was conducted in toluene at 60 °C in the presence of a catalytic amount of AIBN (Table 1, Run 1). After stirring for 8 h, the reaction mixture was cooled to room temperature and then added to

Table 1. Results of Terpolymerization of *cyclo*-$(MA)_5$, PA, and St in Various Feed Ratios or at Various Temperatures

Run	x : y : z[a]	Temp. (°C)	M_w[b]	M_n[b]	M_w/M_n[b]	Yield (%)[c]	m : n : l[d]
1	1 : 1 : 1	60	13 900	10 200	1.4	38	1 : 0.99 : 0.56
2	1 : 1 : 0.11	60	13 800	9 800	1.4	45	1 : 1.00 : 0.06
3	1 : 1 : 0.33	60	11 000	9 300	1.2	39	1 : 1.00 : 0.10
4	1 : 1 : 0.67	60	11 000	7 700	1.4	37	1 : 1.00 : 0.25
5	1 : 1 : 3	60	15 100	11 100	1.4	44	1 : 1.02 : 2.58
6	1 : 1 : 9	60	24 800	15 500	1.6	41	1 : 1.05 : 6.35
7	1 : 0.33 : 1	60				0	
8	1 : 0.67 : 1	60	7 300	6 300	1.2	28	1 : 1.01 : 0.13
9	1 : 2 : 1	60	12 400	10 000	1.2	29	1 : 1.09 : 0.10
10	0.25 : 1 : 1	60	14 900	11 000	1.3	13	1 : 1.09 : 0.26
11	0.5 : 1 : 1	60	14 500	11 400	1.3	22	1 : 1.04 : 0.14
12	2 : 1 : 1	60	8 200	7 300	1.1	5	1 : 1.00 : 0.00
13	1 : 1 : 1	45	19 400	14 900	1.3	37	1 : 1.05 : 0.00
14	1 : 1 : 1	75	11 100	8 400	1.3	41	1 : 1.04 : 0.70
15	1 : 1 : 1	90	13 000	9 700	1.4	37	1 : 1.00 : 0.51

[a] Molar ratio of the fed monomers (MA : PA : St). Refer to Scheme 1. [b] Estimated by GPC analysis in chloroform on the basis of polystyrene standards. [c] Isolated yield after reprecipitation from toluene to hexane, (weight of the obtained polymer) / (total weight of the monomers). [d] Estimated by ^{1}H NMR.

n-hexane to precipitate a polymer. The polymer obtained was purified by reprecipitation from toluene to *n*-hexane twice and freeze-dried for 10 h to yield the polymer **1** as a light yellow powder in 38 % yield. The resulting polymer **1** was highly soluble in common organic solvents including THF, $CHCl_3$, toluene, etc., and easily cast on a glass plate to give a film. The GPC ($CHCl_3$) trace of **1** showed a single peak. The number-average molecular weight of **1**, determined by GPC ($CHCl_3$) using polystyrene standard, was 10 200 (Table 1, Run 1) with polydispersity index of 1.4.

Characterization by ^{1}H and ^{13}C NMR Spectra. Figures 1 and 2 show the ^{1}H and ^{13}C NMR spectra of **1** recorded in $CDCl_3$ at room temperature. Both of the spectra exhibit the peaks attributable to polystyrene in addition to the peaks from poly(vinylene-arsine). No obvious peaks were observed other than those peaks. These observations suggest that the terpolymer **1** was composed of two block segments of poly(vinylene-arsine) and polystyrene (Chart 1, R_1 = H, R_2 = Ph). In the ^{1}H NMR spectrum, two main groups of the peaks associated with chemical shifts at 1.0 – 2.2 and 6.1 – 7.5 ppm can be attributed to the aliphatic groups and the aromatic and vinyl protons, respectively. The assignments of these peaks are given in Figure 1. The integral ratio of these peaks revealed that the composition of **1**

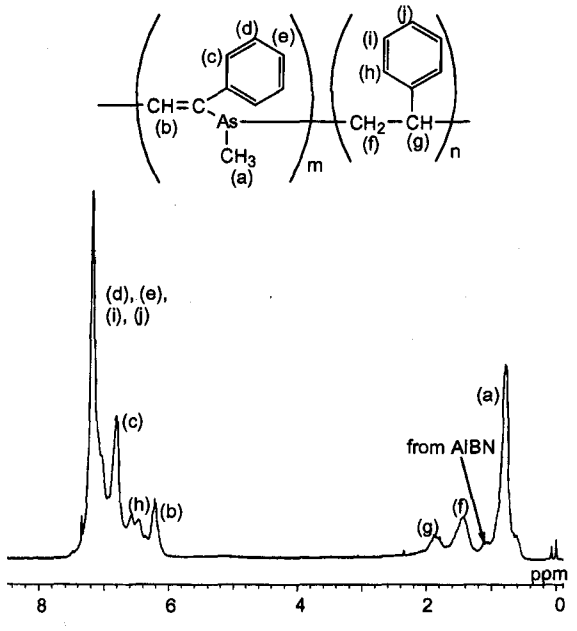


Figure 1. ^{1}H NMR spectrum of **1** recorded in $CDCl_3$.

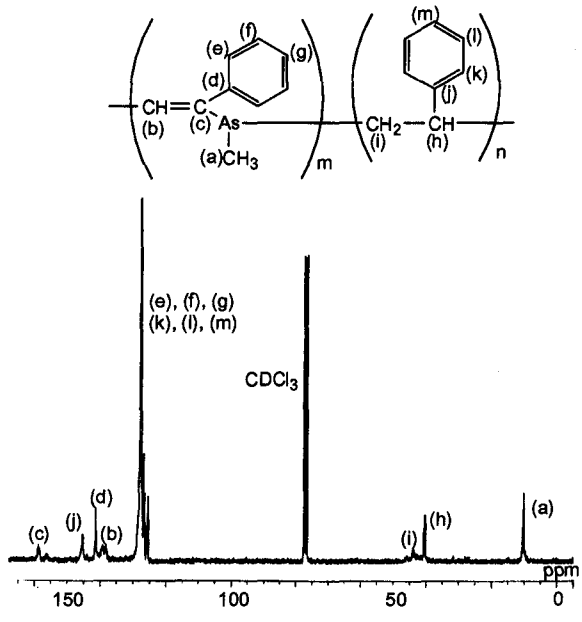


Figure 2. ^{13}C NMR spectrum of **1** recorded in $CDCl_3$.

was MA (methylarsine unit, CH_3As) : PA : St = 1 : 0.99 : 0.56. The molar quantity of MA and PA unit in the terpolymer was almost equal, which also ensured the structure in Chart 1. The content of St unit in the terpolymer was smaller than the monomer feed ratio of St. The ^{13}C NMR spectrum (Figure 2) of **1** shows peaks at 152 - 159 ppm and 138 - 140 ppm attributable to the vinyl carbons. Each area has two peaks derived from the *cis*- and *trans*-isomers. Only one sharp resonance for $AsCH_3$, of which the assignment was supported by the DEPT spectrum, is observed at 10.2 ppm in Figure 2, suggesting that the copolymerization of *cyclo*-$(MA)_5$ with PA proceeded highly alternatingly to produce the poly(vinylene-arsine) segment.

Copolymerization of Two Monomers out of *cyclo*-$(MA)_5$, PA, and St. To investigate the reactivity of *cyclo*-$(MA)_5$, PA, and St to each other, two monomers out of them were treated in the presence of a catalytic amount of AIBN at 60 °C. As reported in Chapter 1, the radical reaction between *cyclo*-$(MA)_5$ and PA produced the alternating copolymer, poly(vinylene-arsine). The treatment of *cyclo*-$(MA)_5$ with St resulted in the formation of purple-black precipitate which was insoluble in all solvents. Since the precipitate was insoluble and fuming in the air, the full-characterization of the mixture should be suspended. It can, however, be presumed from the appearance that the precipitate was linear poly(methylarsine) which stacked with each other to form a ladder structure.[4] No polystyrene or copolymer containing styrene unit was obtained. Though it remains to be seen whether radical species from AIBN reacted with *cyclo*-$(MA)_5$ or St, *cyclo*-$(MA)_5$ inhibited the radical polymerization of St. Stirring a mixture of the equimolar amount of PA and St with a catalytic amount of AIBN in toluene at 60 °C brought about a polymeric material. After reprecipitation from toluene to methanol (yield 9 %), the molecular weight of the copolymer was estimated by GPC ($CHCl_3$, polystyrene standard) and found to be low (M_n = 1 800, with polydispersity index of 1.3). This result suggests that the homo-propagation of St was inhibited by PA which had low homopolymerizability under this condition.

Mechanism of the Terpolymerization. In the terpolymerization system of *cyclo*-$(MA)_5$ with PA and St, the following elementary reactions can be proposed in the initiation and chain-growth reactions:

Initiation

$R\cdot + (MA)_5 \rightarrow \cdot MA\cdot, \cdot MA\text{-}MA\cdot, \cdot MA\text{-}(MA)_n\text{-}MA\cdot$ (1)

$R\cdot + PA \rightarrow R\text{-}PA\cdot$ (2)

$R\cdot + St \rightarrow R\text{-}St\cdot$ (3)

Propagation

$\sim MA\cdot + MA \rightarrow \sim MA\text{-}MA\cdot$ (4)

$\sim MA\cdot + PA \rightarrow \sim MA\text{-}PA\cdot$ (5)

$\sim MA\cdot + St \rightarrow \sim MA\text{-}St\cdot$ (6)

$\sim PA\cdot + MA \rightarrow \sim PA\text{-}MA\cdot$ (7)

$\sim PA\cdot + PA \rightarrow \sim PA\text{-}PA\cdot$ (8)

$\sim PA\cdot + St \rightarrow \sim PA\text{-}St\cdot$ (9)

$\sim St\cdot + MA \rightarrow \sim St\text{-}MA\cdot$ (10)

$\sim St\cdot + PA \rightarrow \sim St\text{-}PA\cdot$ (11)

$\sim St\cdot + St \rightarrow \sim St\text{-}St\cdot$ (12)

Among the three initiation reactions, (2) is improbable due to the low reactivity of PA with the carbon radical from AIBN.[1] Thus, the initiations of the terpolymerization are competitive reactions of (1) and (3). The ^1H NMR spectrum of **1** (Figure 1) showed the peaks due to the terminal isobutyronitrile group from AIBN, which did not appear in that of poly(vinylene-arsine) but in that of polystyrene. This result also ensures that the initialization reaction of the terpolymerization includes the attack of radicals from AIBN on St monomer.

The propagation reactions of (5) and (7) proceed readily as well as (12), which was evidenced in Chapter 1. Since the arsenic-arsenic bond is unstable and easily cleaved to reproduce the arsenic radicals, reaction (4) is excluded from the chain-growth. Though the elementary reactions of (6), (8), (9), (10), and (11) can be included in the propagation reactions of the terpolymerization, the frequencies of them are much lower than those of the other chain-growth reactions, which is presumed by the results of the binary copolymerizations described above. This is also supported experimentally by the ^1H and ^{13}C NMR spectra which suggest the structure of the terpolymer with two block segments,

poly(MA-*alt*-PA) and poly(St). The reactions of (6), (9), (10), and (11) with low frequencies make the connecting point of the two blocks.

Terpolymerization of *cyclo*-$(MA)_5$ with PA and St in Various Monomer Feed Ratios or at Various Temperatures. The radical terpolymerization of *cyclo*-$(MA)_5$, PA, and St using AIBN was carried out in various monomer feed ratios. The results of molecular weights, yields, and terpolymer compositions of the resulting polymers are listed in Table 1. In the Slocombe-plot (Figure 3) based on the results in Table 1, the feed composition (red circle) and the terpolymer composition (blue circle) are shown. As can be seen all blue circles are nearly on the perpendicular line which represents the equimolar amount of the MA and PA units. The ^1H and ^{13}C NMR spectra of the obtained polymers exhibited the peaks of poly(vinylene-arsine) unit and polystyrene unit, suggesting that the terpolymer had the two block segments. In every case the blue circle is located below the corresponding red circle, indicating that the content of St unit in the terpolymer was less than the feed ratio of St. In Run 7 where the feed ratio was MA : PA : St = 1 : 0.33 : 1, no copolymer or terpolymer but purple-black precipitate was obtained. As in the reaction of *cyclo*-$(MA)_5$ and St, MA acted as a polymerization inhibitor. Similarly to this, the radical reaction in Run 12 (feed ratio MA : PA : St = 2 : 1 : 1) yielded the alternating copolymer of MA and PA with no St unit in

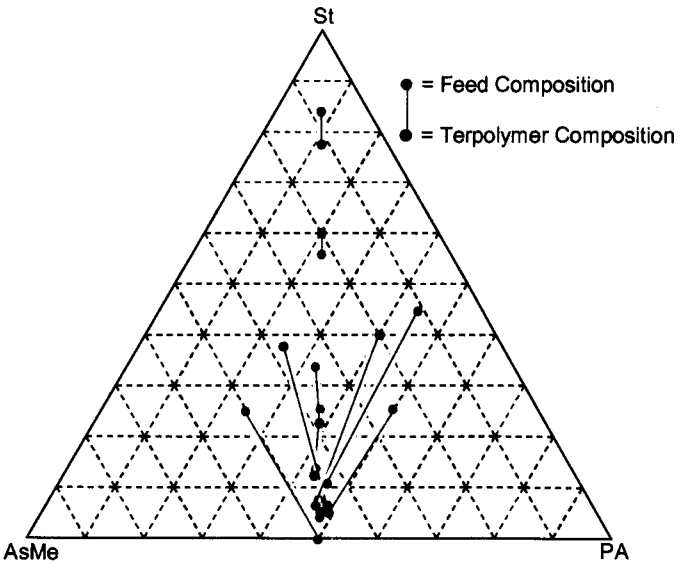


Figure 3. Monomer-terpolymer composition diagram: (●) for monomer feed ratio and (●) for terpolymer composition.

low yield. The terpolymerization in Run 9 (feed ratio MA : PA : St = 1 : 2 : 1) gave the terpolymer with low content of St unit (terpolymer composition MA : PA : St = 1 : 1.01 : 0.13) in comparison with Run 1. Under the condition where an excess amount of PA was employed, the chain-transfer of polymer St radical with PA monomer (propagation (11)) was caused more often than in Run 1.

The terpolymerization of MA with PA and St in the feed ratio 1 : 1 : 1 was performed at various temperatures (Run 1 and 13 – 15). The radical reaction above 60 °C (Run 1, 14, and 15) produced the terpolymer composed of two block segments. The reaction at 45 °C (Run 13), in contrast, resulted in the poly(vinylene-arsine) with no St unit. It turned out that the initiation reaction (1) proceeded in preference to (3) and the chain transfer of MA and PA radical to St (propagation (6) and (9)) was excluded at this temperature.

Optical Properties of the Terpolymers. In accordance with the fact that the terpolymer possesses the poly(vinylene-arsine) unit in the backbone, the terpolymer showed optical properties which are analogous to those of the poly(vinylene-arsine).[1] The solution of the terpolymer **1** in chloroform exhibited not only the strong absorption in the region < 360 nm derived from π–π^* transition but also the weak absorption in the region > 360 nm. The absorption edge was located at around 500 nm. The latter lower energy absorption is attributable to the n–π^* transition in the poly(vinylene-arsine) block.[1] The dilute chloroform solution of **1** exhibited the emission with a maximum peak at 470 nm by irradiation at 470 nm (Figure 4). The excitation spectrum of **1** emitted at 470 nm showed a peak at 388 nm but no absorption in the region < 340 nm (Figure 4). This result suggests

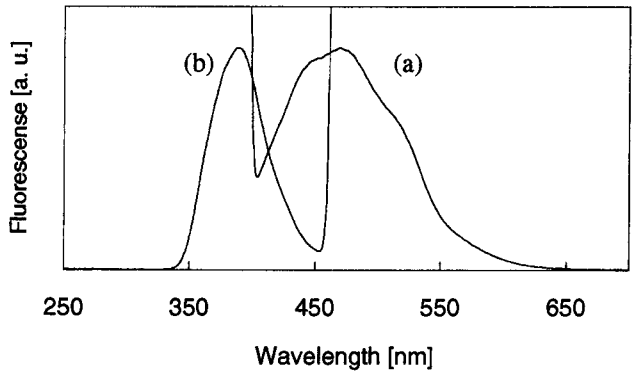


Figure 4. Emission ((a), excited at 388 nm) and excitation ((b), emitted at 470 nm) spectra of **1** recorded in chloroform at room temperature.

that the emission of **1** arises from only the n-π* transition in the poly(vinylene-arsine) segment. Figure 5 presents the emission or excitation peaks as a function of the content of St unit in the terpolymer (Run 1-6). The data reveal that the increase of St unit in the terpolymer causes blue shift of the peaks in both emission and excitation spectra. Though it remains to be seen how long the effective conjugation length of poly(vinylene-arsine) is, the terpolymer with high ratio of St unit has shorter chain of poly(vinylene-arsine) than the effective conjugation length.

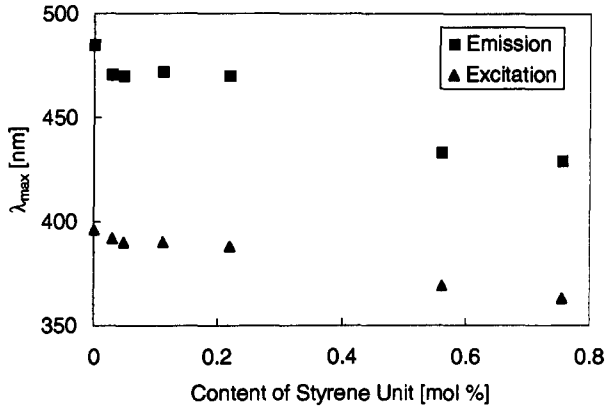


Figure 5. Effect of content of St unit in the terpolymer obtained in Run 1 – 6 on λ_{max} in emission (•) and excitation (•) spectra.

Radical Terpolymerization of *cyclo*-$(MA)_5$, PA, and Other Vinyl or Butadienyl Monomers. Here performed the radical terpolymerization of *cyclo*-$(MA)_5$, PA, and methyl methacrylate (MMA) in the feed ratio MA : PA : MMA = 1 : 1 : 1 (Scheme 3, R_1 = Me, R_2 = COOMe). After the reprecipitation, a polymer was obtained as a light yellow powder (yield 56 %). The polymer showed a single peak in the GPC trace, and the number-average molecular weight using polystyrene standard was 12 500 with the polydispersity index of 1.5. By characterization with ^1H and ^{13}C NMR spectra, the resulting polymer was terpolymer with two block segments, poly(vinylene-arsine) and poly(MMA). The peak area ratio in the ^1H NMR spectrum revealed that the composition of the two blocks was 1 : 0.48. On the other hand, the radical reaction of *cyclo*-$(MA)_5$ with PA and vinyl acetate (VA) under the same condition yielded poly(vinylene-arsine). No poly(VA) or copolymer containing VA unit was obtained, whereas VA can be homopolymerized in toluene at 60 °C with a catalytic

amount of AIBN. Since VA has no substitution group with resonance effect, the reactivity of the vinyl group of VA is low compared to that of St or MMA. Thus, no initiation reaction of AIBN with VA or chain-transfer reaction to VA took place.

2,3-Dimethyl-1,3-butadiene (DB) was also employed as a monomer instead of the vinyl monomer and the radical terpolymerization was carried out with *cyclo*-$(MA)_5$ and PA using AIBN in toluene at 55 °C in the monomer feed ratio of MA : PA : DB = 1 : 1 : 1 (Scheme 4). After the reprecipitation a polymeric material (**2**) was obtained as a white powder in 34 % yield. The resulting polymer showed a single peak in the GPC trace. The GPC analysis using polystyrene standards estimated the number-average molecular weight of **2** to be 6 900 with polydispersity index of 1.8 (Table 2, Run 16). Figure 6 shows ^{1}H NMR spectrum of **2**.[5] In addition to the peaks due to the aromatic and vinyl protons and the methyl group attached to the arsenic atom, two peaks are observed in the aliphatic region of the spectrum. The ^{13}C NMR spectrum of **2** (Figure 7) also exhibits a few aliphatic peaks besides the peaks identical to poly(vinylene-arsine). One of the additional peaks is assigned to As*C*H_3 next to the butadienyl unit.[6] From the peak area ratio in the ^{1}H NMR spectrum, the terpolymer composition of **2** is calculated to be MA : PA : DB = 1 : 0.91 : 0.10 (Table 2, Run 17). In contrast to **1**, the content of MA in the terpolymer was not same as that of PA but almost same as the sum of the content of PA and DB.

Scheme 4

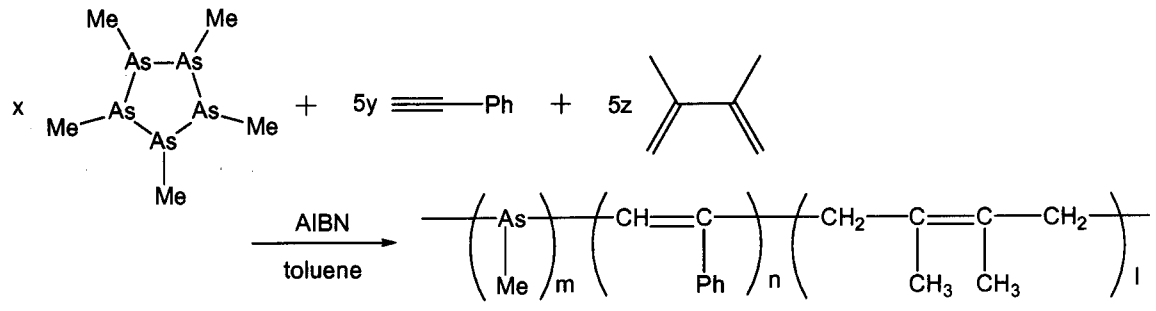


Table 2. Results of Terpolymerization of *cyclo*-$(MA)_5$, PA, and DB in Various Feed Ratios.

Run	x : y : z[a]	Temp.(°C)	M_w[b]	M_n[b]	M_w/M_n[b]	Yield (%)[c]	m : n : l[d]
16	1 : 1 : 1	55	12 700	6 900	1.8	34	1 : 0.91 : 0.10
17	1 : 1 : 2	55	9 000	5 900	1.5	27	1 : 0.84 : 0.14
18	1 : 1 : 3	55				Trace	

[a] Molar ratio of the fed monomers (MA : PA : DB). [b] Estimated by GPC analysis in chloroform on the basis of polystyrene standards. [c] Isolated yield after reprecipitation from toluene to hexane, (weight of the obtained polymer) / (total weight of the monomers). [d] Estimated by ^1H NMR.

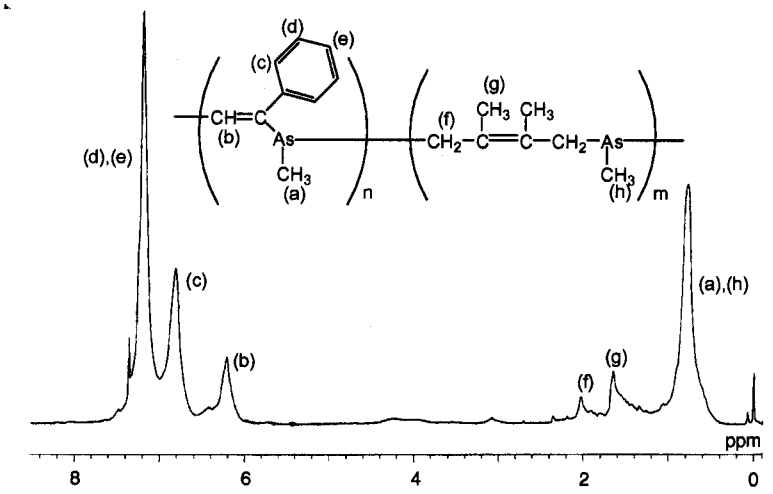


Figure 6. ^1H NMR Spectrum of **2** recorded in $CDCl_3$.

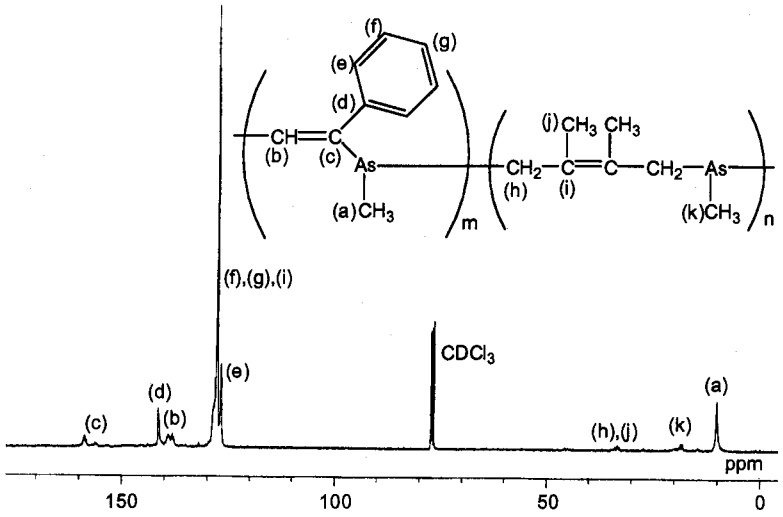
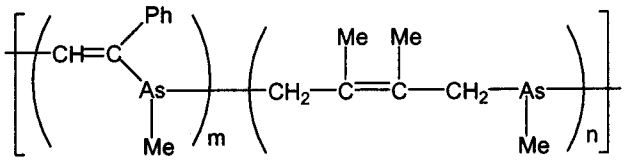


Figure 7. ^{13}C NMR spectrum of **2** recorded in $CDCl_3$

The radical terpolymerization in Run 17 in Table 2, where two times molar amount of DB as that of PA was employed, produced the terpolymer with the composition MA : PA : DB = 1 : 0.84 : 0.14. The terpolymer obtained here also contained about 50 mol% of MA unit. From these results, it is assumed that the terpolymer possesses the structure with alternating sequences of MA unit and PA or DB unit (Chart 2) in a similar manner with the complex-radical terpolymerization of acceptor-donor-acceptor or donor-acceptor-donor monomer systems.[3] Whereas the radical reaction of *cyclo*-$(MA)_5$ with St yielded the poly(MA) with the ladder structure, the reaction of *cyclo*-$(MA)_5$ and DB with heat or under the irradiation of an incandescent lamp produced a cyclic diarsine compound, 1,2,4,5-tetramethyltetrahydrodiarsine.[7] The treatment of the cyclic compound with PA in the presence of AIBN or irradiation of the incandescent lamp produced no polymeric material. It turns out, therefore, that the terpolymerization of *cyclo*-$(MA)_5$ with PA and DB proceeded without the cyclization. It can be presumed that the "ternary alternating terpolymerization" of MA, PA, and DB was achieved by the preferential reactivity of PA and DB polymer radical to MA and that of MA polymer radical to PA and DB. The terpolymerization in the feed ratio MA : PA : DB = 1 : 1 : 3 resulted in no polymeric material (Table 2, Run 18) since the high concentration of butadienyl radical caused easily the recombination reaction to terminate the polymerization.

Chart 2



Summary

Here describes a radical terpolymerization of *cyclo*-$(MA)_5$, PA, and a vinyl monomer. In the case of employing St or MMA as a vinyl monomer, a terpolymer with poly(vinylene-arsine) and poly(St) or poly(MMA) segments in the backbone was obtained. The terpolymer was formed by chain-transfer type reactions of polymer MA or PA radical with the vinyl monomer and of polymer vinyl radical with MA or PA. Though the ratio of

the chain-transfer reactions is unclear, this terpolymerization system is unique in the respect that it gave a terpolymer with two kinds of blocks by the simple treatment of three kinds of monomers. One of the blocks is an alternating copolymer and the other is a homopolymer. The obtained terpolymer showed fluorescent properties due to the poly(vinylene-arsine) block and the emission peak could be tuned by varying the monomer feed ratio. The radical reaction of *cyclo*-$(MA)_5$ with PA and DB, in contrast, produced the random copolymer with MA-PA and MA-DB units. These terpolymerizations are useful for the synthesis of organoarsenic polymer with various functional groups.

Experimental Section

Materials. Unless otherwise noted, all reagents and chemicals were purchased from Wako Pure Chemical Industries, Ltd. Dehydrated toluene (water < 30 ppm) was bubbled with a stream of nitrogen before use. Dehydrated *n*-hexane (water < 30 ppm) was used without further purification. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Styrene (St), methyl methacrylate (MMA), and vinyl acetate (VA) were distilled under reduced pressure before use. Phenylacetylene (PA) and 2,3-dimethyl-1,3-butadiene (DB) were purchased from Aldrich and purified by distillation under reduced pressure. Pentamethylcyclopentaarsine (*cyclo*-$(MA)_5$) was synthesized using a literature procedure.[7]

Equipment. All reactions and manipulations were carried out under an atmosphere of prepurified nitrogen using Schlenk techniques. ^1H and ^{13}C NMR spectra were obtained using a JEOL JNM-EX270 instrument (270 and 67.5 MHz, respectively) for solutions in $CDCl_3$ and were referenced to $SiMe_4$ (TMS). UV-vis spectra were measured on a JASCO V-530 spectrometer, and samples were analyzed in $CHCl_3$ at room temperature. Fluorescence emission spectra were recorded on a Perkin-Elmer LS50B luminescence spectrometer, and samples were analyzed in $CHCl_3$ at room temperature. Gel permeation chromatography was carried out on a TOSOH UV-8011 and RI-8000 (Shodex K-803L column) using $CHCl_3$ as an eluent after calibration with standard polystyrene. Gas chromatography (GC) analyses were carried out on a SHIMADZU GC-17A using helium gas as a carrier gas.

Polymerization. Terpolymerization of *cyclo*-(MA)$_5$, PA, and St with AIBN as a Radical Initiator. To a solution of *cyclo*-(MA)$_5$ (0.569 g, 1.27 mmol) and St (0.658 g, 6.33 mmol) in toluene (2.0 mL) was added a solution of PA (0.646 g, 6.33 mmol) and AIBN (0.030 g, 0.18 mmol) in toluene (0.5 mL) at room temperature. The mixture was immediately heated at 60 °C and stirred. The flask for PA and AIBN was rinsed with toluene (0.5 mL) and the resulting toluene solution was added to the reaction mixture. After stirring for 8 h at 60 °C, the mixture was cooled at room temperature and then poured into *n*-hexane to precipitate a polymeric material, which was purified twice by reprecipitation from toluene to *n*-hexane. After freeze-drying for 10 h, the polymer was obtained as a light yellow powder (0.726g, 38 % yield). ^{1}H NMR (δ, ppm): 6.95-7.50 (ArH_m and ArH_p of PA, ArH_m and ArH_p of St), 6.70-6.95 (ArH_o of PA), 6.40-6.70 (ArH_o of St), 6.05-6.40 (*(E)*- and *(Z)*-C=C*H*), 1.70-2.00 (-CH_2-), 1.25-1.70 (-CH-), 1.05-1.20 (-CH_3 from AIBN), 0.50-1.05 (-CH_3). ^{13}C NMR (δ, ppm): 158.8, 152.5 (*(E)*- and *(Z)*-*C*=CH), 145.1 (CH_2-CH-C_{Ar} of St), 141.4 (CH=C-C_{Ar} of PA), 139.2, 138.2 (*(E)*- and *(Z)*-C=*C*H), 127-130 ($C_{Ar}H_m$ and $C_{Ar}H_p$ of PA, $C_{Ar}H_m$ and $C_{Ar}H_p$ of St), 126.7 ($C_{Ar}H_o$ of PA), 125.6 ($C_{Ar}H_o$ of St), 41-46 (-CH_2-), 40.4 (-CH-), 10.2 (-CH_3).

Terpolymerization of *cyclo*-(MA)$_5$, PA, and MMA. In toluene (3.0 mL in total), *cyclo*-(MA)$_5$ (0.561 g, 1.25 mmol), MMA (0.625 g, 6.24 mmol), PA (0.637 g, 6.24 mmol), and AIBN (0.030 g, 0.18 mmol) were employed. The terpolymerization and purification were carried out as described above and the corresponding polymer was obtained (1.02 g, 56 % yield). ^{1}H NMR (δ, ppm): 7.08-7.58 (ArH_m, ArH_p), 6.82 (ArH_o), 6.05-6.55 (*(E)*- and *(Z)*-C=C*H*), 3.60 (-OCH_3), 1.80-2.20 (C-CH_3), 1.2-1.6 (-CH_3 from AIBN), 1.03 (-CH_2-), 0.84 (As-CH_3).

Terpolymerization of *cyclo*-(MA)$_5$, PA, and DB. In toluene (3.0 mL in total), *cyclo*-(MA)$_5$ (0.561 g, 1.25 mmol), PA (0.637 g, 6.23 mmol), DB (0.512 g, 6.23 mmol), and AIBN (0.030 g, 0.18 mmol) were employed. The terpolymerization and purification were carried out as described above and the corresponding polymer was obtained (0.578 g, 34 % yield). ^{1}H NMR (δ, ppm): 7.05-7.60 (ArH_m and ArH_p), 6.65-7.05 (ArH_o), 6.05-6.60 (*(E)*- and *(Z)*-C=C*H*), 2.02 (-CH_2-), 1.25-1.70 (-CH-), 1.65 (C-*C*H_3), 0.78 (As-*C*H_3). ^{13}C NMR (δ, ppm): 148.2. 145.8 (*(E)*- and *(Z)*-*C*=CH), 141.6 (CH=C-C_{Ar}), 139.4, 138.4 (*(E)*- and

(Z)-C=*C*H), 126-131 ($C_{Ar}H_o$, $C_{Ar}H_m$, and $C_{Ar}H_p$ of PA, -*C*Me=*C*Me-), 33.1 (-CH_2-), 18.5 (C-*C*H_3), 10.2 (As-CH_3).

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Chapter 6

Synthesis and Properties of Cross-Linked Poly(vinylene-arsine)s

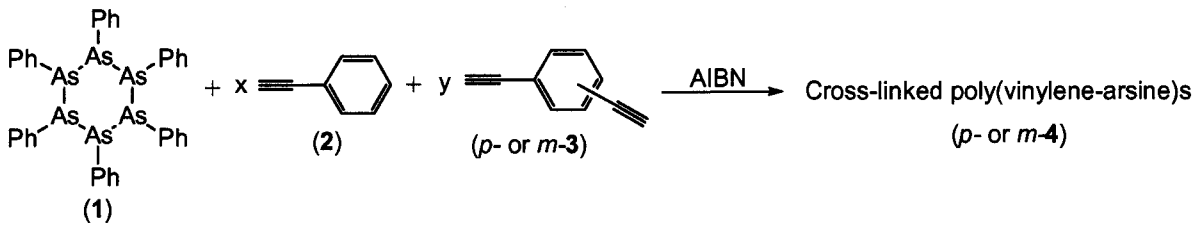
Abstract: Cross-linked poly(vinylene-arsine)s (**4**) were synthesized by a free-radical terpolymerization of hexaphenylcyclohexaarsine (**1**), phenylacetylene (**2**), and *p*- or *m*-diethynylbenzene (*p*- or *m*-**3**) at different compositions in the presence of a catalytic amount of AIBN. The number-average molecular weights of the resulting polymers were a few thousands estimated by gel permeation chromatography (GPC) analysis. By gas chromatography (GC) analysis *p*-**3** was found to be more reactive during the polymerization than *m*-**3** and the resulting cross-linked polymer (*p*-**4**) showed lower solubility than that of *m*-**4**. The cross-linked poly(vinylene-arsine)s showed higher glass transition temperature in the measurement of differential scanning calorimetry (DSC) and more red-shifted emission in chloroform solution than that of the linear poly(vinylene-arsine). These properties could be tuned by varying the monomer feed ratio.

Introduction

Organic / inorganic hybrid polymers, i. e., macromolecules in which inorganic elements play the key role in the backbone, possess characteristic properties different from "organic polymers" with backbones consisting of either only carbon or carbon in combination with oxygen or nitrogen[1]. Chapter 1, as a new synthetic route to inorganic polymers, described the ring-collapsed radical alternating copolymerization of arsenic homocyclic compounds with acetylenic compounds using 2,2'-azobisisobutyronitrile (AIBN) as a radical initiator to produce the corresponding alternating copolymer, poly(vinylene-arsine).[2] The obtained polymer is the first example of the soluble polymer having arsenic atoms in the main chain with a well-defined structure. Regardless of the feed ratio of two monomers, the copolymerization produced the polymer with 1 : 1 alternating structure of arsenic unit and vinylbenzene unit in the backbone. The extension of the conjugation length via lone pair on the arsenic atoms in the polymer chain was proved by the UV-vis absorption spectrum. The alternating copolymer showed fluorescent properties attributable to the n-π^* transition in the backbone. Besides the optical properties, the poly(vinylene-arsine)s can have many functionalities, for example, to form a polymer complex with a various kinds of transition metals and to act as a reducing agent due to the lone pair on the arsenic atom.

On the other hand, conjugated cross-linked polymer networks (gels) have been studied owing to the unique properties, such as environmental responses[3] and enhanced conductivities.[4] This chapter describes the synthesis of cross-linked poly(vinylene-arsine)s by the radical terpolymerization of cyclooligoarsine, phenylacetylene, and *p*- or *m*-diethynylbenzene (Scheme 1). If each polymer chain with the structure of vinylene-arsine is cross-linked by one another, the electrical structure would be affected due

Scheme 1



to the enhancement of the interchain interaction, and thus more extension of the conjugation length would be expected. In addition, closely packed structure might improve the thermal stability of the poly(vinylene-arsine)s.

Results and Discussion

Synthesis of Cross-Linked Poly(vinylene-arsine). A typical terpolymerization procedure (Run 3 in Table 1) of hexaphenylcyclohexaarsine (**1**), phenylacetylene (**2**), and *p*- or *m*-diethynylbenzene (**3**) was conducted as follows. Under a nitrogen atmosphere, a mixture of **1**, **2**, *p*-**3**, and AIBN at a feed ratio of 1 : 3 : 1.5 : 0.17 was stirred in refluxing benzene for 12 h. In this monomer feed ratio, the molar ratio of the phenylarsine unit (PhAs) with total ethynyl group was unity. In the early stage of the polymerization, the reaction mixture was heterogeneous due to the insolubility of **1** in benzene. Within about 30 minutes after the initiation of the polymerization, the reaction mixture became homogeneous, suggesting that the ring structure of **1** collapsed completely. The reaction mixture maintained the homogeneity until the polymerization was ceased. After stirring, the reaction mixture was poured into *n*-hexane to precipitate the polymeric material. The resulting polymer was purified by reprecipitation from benzene to *n*-hexane three times, and freeze-dried for 10 h to yield the corresponding cross-linked poly(vinylene-arsine) as a yellow powder in 51 %. The relatively low yield of the isolated polymer was due to the removal

Table 1. Results of Copolymerization

Run	**3**	Feed Ratio **2 / 3**	M_w[a]	M_n[a]	M_w/M_n[a]	Yield (%)[b]	Solubility[c]	T_g[d] (°C)
1		6.0 / 0	5600	3900	1.4	35	soluble	92.9
2	*p*-	5.0 / 0.5	3700	1900	1.9	29	soluble	92.9
3	*p*-	3.0 / 1.5	11800	2800	4.2	51	soluble[e]	101.7
4	*p*-	2.0 / 2.0	ND[f]	ND	ND	62	insoluble	104.9
5	*m*-	3.0 / 1.5	7800	2700	2.9	48	soluble	99.2
6	*m*-	2.0 / 2.0	8000	2600	3.1	54	soluble	103.7

[a] Determined by GPC analysis (DMF, polystyrene standards). [b] Isolated yields after reprecipitation into *n*-hexane. [c] Solubility of 250 mg of the polymer in 5.0 mL of benzene, chloroform, and DMF. [d] Determined by DSC measurement. [e] Decreased solubility in benzene. [f] ND = not determined.

of low molecular weight products by the reprecipitation. The obtained polymer was soluble in common organic solvents such as benzene, toluene, chloroform, and DMF owing to the low cross-linking density, and showed a single peak on the GPC (DMF as a solvent) trace. The number-average molecular weight of the obtained polymer was estimated by the GPC analysis and found to be 2 800 (*vs* polystyrene standards) with the polydispersity index (PDI) of 4.2. The higher value of PDI of the resulting polymer than that of the linear poly(vinylene-arsine) (Run 1 in Table 1) suggests the cross-linked polymer structure. ^{1}H NMR and ^{13}C NMR spectra of the obtained polymer supported the polymer structure of vinylene-arsine. The absence of an obvious peak around 3 ppm in the ^{1}H NMR spectrum indicates that the cross-linked polymer possesses no residue of ethynyl groups.

Terpolymerization in Various Monomer Feed Ratios. The terpolymerizations were carried out at different compositions of **1**, **2**, and *p*- or *m*-**3** with a catalytic amount of AIBN in refluxing benzene to investigate their effects in the polymerization behavior and the polymer properties. The monomer feed ratios, the molecular weights, yields, and solubility of the obtained polymers are summarized in Table 1. In all cases the same molar amount of the PhAs unit as that of total ethynyl group was employed. In Run 4 in which **2** and *p*-**3** were employed with a molar ratio of 1 : 1, the reaction mixture became heterogeneous due to the deposition of the insoluble polymeric material within 2 h after the terpolymerization was initiated. The GPC analyses showed that the polydispersity index (PDI) of the polymers increased with the concentration of the diethynylbenzene in the terpolymerization. This result suggests that the diethynylbenzene acted as a cross-linking agent and cross-linking points in the polymer increased with the feed ratio of diethynylbenzene. All of the copolymers except that of Run 4 were soluble in common organic solvents (Table 1). Apparently, the copolymers from *p*-**3** are of lower solubilities than those from *m*-**3**, indicating that the copolymers from *p*-**3** possess more cross-linking points than those from *m*-**3**. All of the polymers except for that of Run 4 were analyzed by ^{1}H and ^{13}C NMR spectroscopies and their main-chain structures of vinylene-arsine were supported. Though the polymer obtained in Run 4 was insoluble and difficult to be characterized, it must be the cross-linked poly(vinylene-arsine) as well as others. Since the polymer in Run 4 possessed more

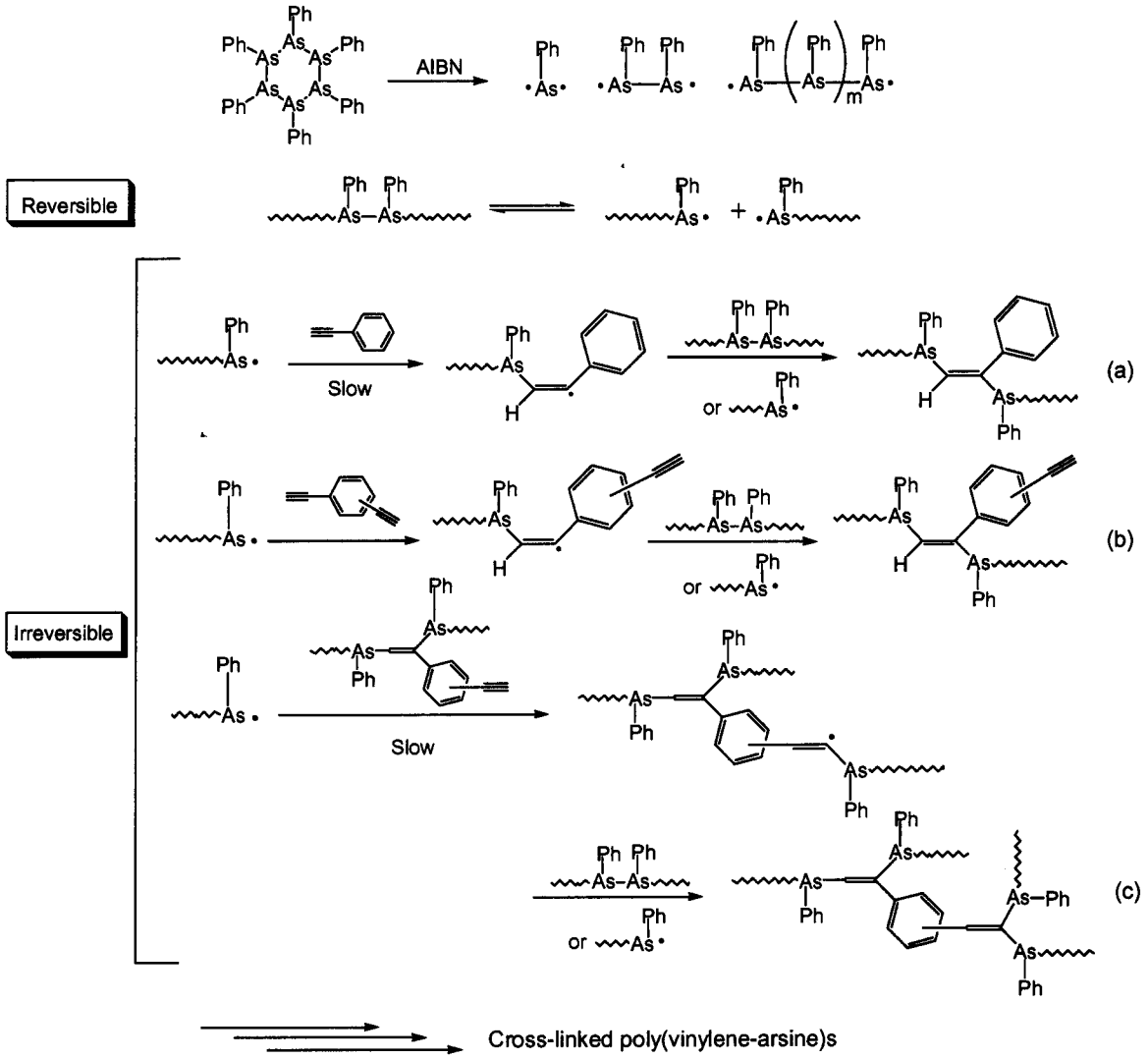
cross-linking points than others, it showed a lower solubility and deposit during the terpolymerization.

The polymer films were made by letting a few drops of the polymer solutions except for that of Run 4 in chloroform (250 mg of the polymer in 5.0 mL of chloroform) stand dried on the slip glasses at room temperature. All the terpolymers exhibited a film-forming property. The degree of the difficulty of the films to be peeled off from the slip glasses was increased in the following order; polymer film of Run 1 ≈ of Run 2 < of Run 3 and of Run 5 < of Run 6. The same order is observed for increasing concentration of diethynylbenzene in the copolymerization. Thus, incorporating diethynylbenzene in the copolymerization yields polymers which exhibit improved film-forming property. The polymers with the more cross-linking points possess the larger weight-average molecular weight, and hence the more improved processability.

Terpolymerization Mechanism. The mechanism of the present terpolymerization should be the same as that of the linear copolymers except that diethynylbenzene participates in the rate-determining step in the polymerization (Scheme 2).[2] First, AIBN cleaved the arsenic-arsenic bond of **1** to produce arsenic radicals. Second, the homolysis of the other arsenic-arsenic bonds proceeded spontaneously due to their instability by the destruction of the quite stable six-membered-ring structure. In competition with this reaction, the arsenic radical added to **2** (path (a)), *p*- or *m*-**3** (path (b)), or the ethynyl group at the polymer side chain (path (c)) to give a vinyl radical. Due to the instability of the produced vinyl radical, this addition is the rate-determining step of the present polymerization. Next the vinyl radical reacted immediately with the arsenic-arsenic bond or with the arsenic radical to form a new carbon-arsenic bond.

The radical terpolymerization of **1**, **2**, and *p*- or *m*-**3** in the feed ratio of 1 : 3.0 : 1.5 was carried out in the presence of *n*-dodecane as a reference material to monitor the amount of consumption of the monomers **2** and *p*- or *m*-**3** by using gas chromatography (GC) analysis. All of the experiments were performed three times, and the average values are presented with error bars in Figure 1. In both cases the diethynylbenzenes (*p*- and *m*-**3**) were consumed much faster than phenylacetylene. When comparing *p*- and *m*-**3**, it is the former that is more reactive than the latter. The difference in the reactivity between *p*- and

Scheme 2



m-diethynylbenzene was obvious during the first hour of the reaction, reaching as high as 30 % after 15 minutes since the reaction started. It is already described in chapter 3 that the reactivity of acetylenic compounds with the arsenic radical becomes higher when the acetylenic monomer bore a conjugated substitution. The unstable vinyl radical was stabilized by the resonance effect and thus its formation (rate-determining step) was promoted. The resonance stabilization acts much more effectively with a *p*-conjugated substitution than a *m*-substitution. Therefore the consumption of *p*-**3** was faster than that of *m*-**3** and, in addition, than two times of the consumption rate of **2**. The ethynyl group at the side chain of the polymer from *p*-**3** should be more reactive than that of **2** and consume predominantly.

This is consistent with the fact that ^{1}H NMR of Run 3 showed no peaks assigned to acetylenic protons. When comparing the reactivity of the residue ethynyl group at the side chain of the polymer from *p*-**3** and from *m*-**3**, the former should be higher than the latter due to the more efficient resonance effect. Therefore, *p*-**3** acts as a more effective cross-linker than *m*-**3** during the terpolymerization. The final conversion ratio of **2** with *p*- or *m*-**3** (Figure 1) revealed that the ratio of diethynylbenzene unit in the polymer structure is higher in the polymer from *p*-**3** than that from *m-3*.

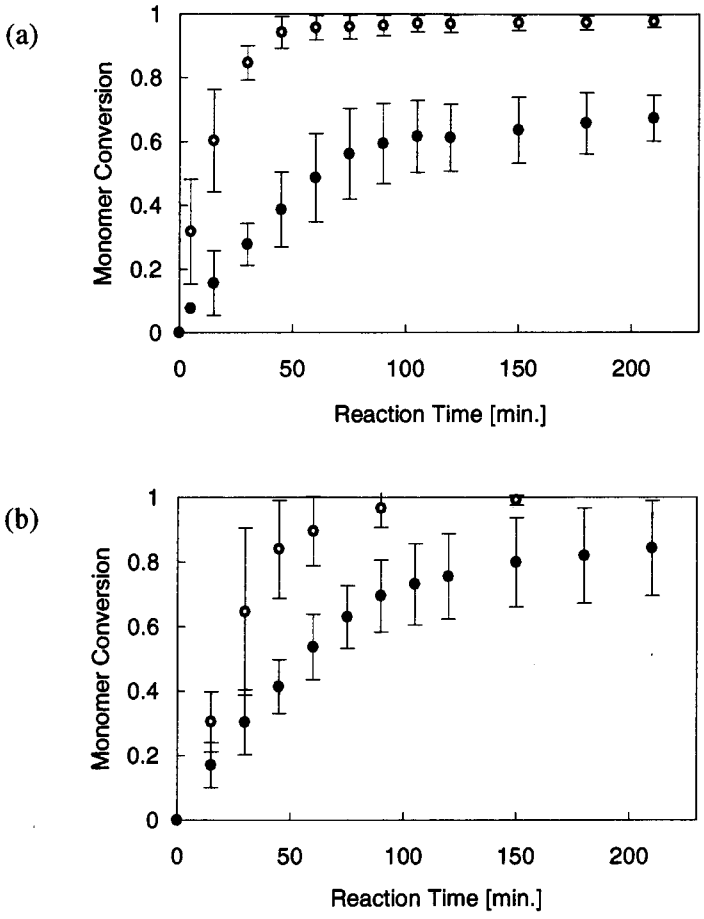


Figure 1. Time-conversion plot of (a) **2** (●) and *p*-**3** (○) and (b) **2** (●) and *m*-**3** (○) during the terpolymerization with **1** in the feed ratio of **1** : **2** : *p*- or *m*-**3** = 1 : 3 : 1.5.

Thermal and Optical Properties of the Cross-Linked Poly(vinylene-arsine)s. To investigate the thermal properties of the obtained cross-linked polymers, the DSC analyses were carried out under nitrogen atmosphere. The values of glass transition temperatures (T_g) are listed in Table 1. As expected, the T_g value increases with increasing the content of the cross-linker, diethynylbenzene, and when the feed ratio of the *p*- and *m*-**3** was same (Table 1, Run 2 *vs* Run 5 and Run 3 *vs* Run 6) the polymers from *p*-**3** showed higher T_g than those from *m*-**3**. This indicates that *p*-**3** acts as a cross-linking agent more efficiently than *m*-**3**. All of the resulting polymers were stable in the solid state at room temperature. No decrease of the molecular weight or no change of the structure was observed even after exposing them to air for several months.

In the UV-vis spectra measured in diluted chloroform solutions, the cross-linked polymers exhibited not only strong absorption in the UV region derived from a π–π^* transition of C=C but also small absorption in the visible region as observed in that of the linear poly(vinylene-arsine). The lower energy absorption was attributable to a delocalized n–π^* transition in the backbone of the polymer. . The absorption edges of the obtained polymers were located around 500 nm.

The fluorescent emission spectrum of the polymer in Run 3 (Figure 2; in chloroform at room temperature; excitation wavelength at 394 nm) showed an emission in the blue region with a peak at 473 nm. The location of the emission and excitation peak maxima are

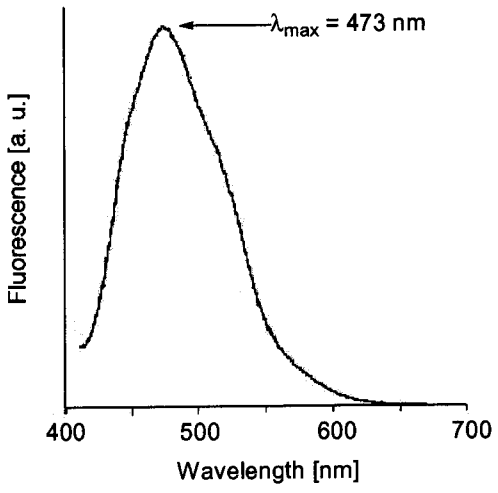


Figure 2. Fluorescence spectrum of the polymer of Run 3 excited at 394 nm recorded in chloroform at 25 °C.

summarized in Table 2, Run 2-6. Those peaks of the cross-linked polymers were red-shifted compared to those of linear poly(vinylene-arsine) (Table 2, Run 1). The favorable interchain interaction of the cross-linked polymers and the extension of the effective conjugation length through the conjugated cross-linking bond resulted in the narrower band gap. The longer extension of the conjugation path by *p*-substituted cross-linker than by *m*-substituted one (Table 2, Run 3 *vs* Run 5 and Run 4 *vs* Run 6) might be derived from the more efficient resonance effect of the conjugated *p*-substitution.

Table 2. Emission and Excitation Peak Maxima

Run[a]	**3**	Feed Ratio **2 / 3**	Emission λ_{max} / nm (Excitation wavelength / nm)	Excitation λ_{max} / nm (Emission wavelength / nm)
1		6.0 / 0	437 (375)	375 (437)
2	*p*-	5.0 / 0.5	473 (394)	394, 340 (473)
3	*p*-	3.0 / 1.5	470 (392)	392 (470)
4	*p*-	2.0 / 2.0	ND[b]	ND
5	*m*-	3.0 / 1.5	465 (392)	392 (465)
6	*m*-	2.0 / 2.0	464 (391)	391 (464)

[a] Measured in chloroform at 25 °C. [b] ND = not determined.

Summary

It is verified in this chapter that incorporating *p*- or *m*-diethynylbenzene as a cross-linking agent in the radical polymerization of phenylacetylene and hexaphenylcyclohexaarsine using AIBN as a radical initiator yields cross-linked poly(vinylene-arsine)s. In comparison with the linear poly(vinylene-arsine), the present cross-linked polymers showed more improved film-forming properties, higher glass transition temperatures, and more red-shifted emissions, while the solubilities in organic solvents became lower. These properties can be controlled by varying the monomer feed ratio. The GC analysis revealed that *p*-diethynylbenzene was more reactive than *m*-diethynylbenzene during the terpolymerization due to the higher

resonance stabilization of the vinyl radical, and thus acted as more effective cross-linking agent.

Experimental Section

Materials. Unless otherwise noted, all reagents and chemicals were purchased from Wako Pure Chemical Industries, Ltd. Toluene (water < 30 ppm) was bubbled with a stream of nitrogen before use. *n*-Hexane (water < 30 ppm), methanol (water < 50 ppm), and *n*-dodecane were used without further purification. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Phenylacetylene (**2**) was purchased from Aldrich and purified by distillation under reduced pressure. *p*-Diethynylbenzene (*p*-**3**) was obtained from Tokyo Kasei, Inc. and sublimed under reduced pressure. *m*-Diethynylbenzene (*m*-**3**) was used as received from Tokyo Kasei, Inc. Hexaphenylcyclohexaarsine (**1**) was synthesized using a literature procedure.[5]

Instruments. All reactions were carried out under an atmosphere of prepurified nitrogen using Schlenk techniques. ^{1}H and ^{13}C NMR spectra were obtained using a JEOL JNM-EX270 instrument (270 and 67.5 MHz, respectively) for solutions in $CDCl_3$ and were referenced to $SiMe_4$ (TMS). Gel permeation chromatographic (GPC) analyses were carried out on a Tosoh 8020 instrument with a TSH-gel Alpha 3000 column with DMF solution containing 10mM LiBr as an eluent after calibration with polystyrene standards. Gas chromatography (GC) analyses were carried out on a SHIMADZU GC-17A using helium gas as a carrier gas. UV-vis spectra were measured on a JASCO V-530 spectrometer with the samples being analyzed in $CHCl_3$ at room temperature. Fluorescence emission spectra were recorded on a Perkin-Elmer LS50B luminescence spectrometer with the samples being analyzed in $CHCl_3$ at room temperature. Differential scanning calorimetry (DSC) thermograms were obtained with a DSC200, Seiko Instruments Inc., with the heating rate of 10 $^{\circ}Cmin^{-1}$ under nitrogen atmosphere.

Synthesis of Cross-Linked Poly(vinylene-arsine)s. A typical experimental procedure is as follows. Under a nitrogen atmosphere, a benzene solution (0.5 mL) of AIBN (0.009 g, 0.05 mmol) was added to a refluxing solution of phenylacetylene (**2**) (0.1 g, 0.9 mmol), hexaphenylcyclohexaarsine (**1**) (0.27 g, 0.30 mmol), and *p*-diethynylbenzene (*p*-**3**) (0.06 g,

0.45 mmol) in benzene (4.5 mL). After being stirred for 12 h, *n*-hexane was poured into the reaction mixture to precipitate the product, which was then purified three times by reprecipitation from benzene to *n*-hexane. After freeze-drying for 10 h, the corresponding cross-linked polymer (*p*-**4**) was obtained as a yellow powder (0.23 g) in 51% yield. ^{1}H NMR (δ in $CDCl_3$, ppm): 5.8 – 8.2 (C=CH, ArH); ^{13}C NMR (δ in $CDCl_3$, ppm): 126–128, 129-131 ($C_{Ar}H$), 131–133 (*C*H=C), 134-135 (*C*-C_{Ar}, C_{Ar}-As), 136-144 (CH=*C*).

GC Analysis of the Reaction Mixture during the Terpolymerization. The radical terpolymerization of **1**, **2**, and **3** using AIBN in the same feed ratio as above was carried out in the presence of *n*-dodecane (0.10 mL) as a standard material. The moment of the addition of a benzene solution of AIBN was defined as the start time of the copolymerization. During the polymerization, a small amount of the reaction mixture was siphoned, diluted with benzene, and analyzed by GC. The consumption rates of **2** and **3** were calculated from the peak area ratios of **2** and **3** with *n*-dodecane.

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Chapter 7

Synthesis of Poly(vinylene-phosphine): Ring-Collapsed Radical Alternating Copolymerization (*RCRAC*) of Cyclooligophosphine with Phenylacetylene

Abstract: A novel conjugated polymer containing phosphorus atom in the main chain, poly(vinylene-phosphine), was synthesized by ring-collapsed radical alternating copolymerization (*RCRAC*) of a cyclooligophosphine and phenylacetylene. Polymerization was conducted as follows. Under a nitrogen atmosphere, a benzene solution of 2,2'-azobisisobutyronitrile (AIBN) was added to a refluxing solution of pentamethylcyclopentaphosphine, *cyclo*-$(MP)_5$, and phenylacetylene (PA) in benzene. After stirring the reaction mixture for 8 h, the resulting polymer was purified by reprecipitation into *n*-hexane three times and freeze-dried for 10 h to yield the corresponding poly(vinylene-phosphine) **1** as a bright yellow powder. From gel permeation chromatographic analysis (chloroform, PSt standards), the number-average molecular weight of the polymer **1** was found to be 2 500. The polymer **1** was readily soluble in common organic solvents such as THF, chloroform and benzene. The structure of the polymer **1** was supported by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopies. The UV-vis absorption spectrum of the polymer **1** in chloroform showed small absorption at a visible region attributable to the n-π^* transition in the main chain, besides strong benzene-ring absorption at a UV region. The fluorescence emission spectrum of a dilute chloroform solution of the polymer **1** showed an emission peak at 470 nm. In the excitation spectrum of **1** monitored at 470 nm, the absorption peaks were observed at 400 and 430 nm corresponding to the n-π^* transition.

Introduction

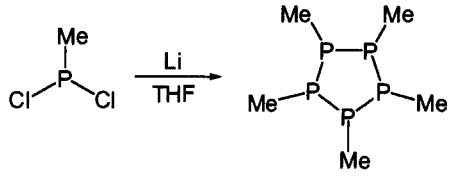
The synthesis of macromolecules possessing inorganic elements in the backbone provides a substantial synthetic challenge but is motivated by the possibility of accessing new materials with interesting and useful properties.[1] Traditional synthetic protocols of organic polymers that involve a chain-growth mechanism such as addition polymerization are difficult to use for inorganic polymer synthesis, since suitably reactive but stable multiple bonds involving inorganic elements are generally difficult to prepare.[2] In contrast to the situation for unsaturated organic molecules (olefins, acetylenes, butadienes, etc.), the isolation of stable species with multiple bonds between inorganic elements or between an element and a carbon usually requires the presence of sterically hindered substituents on the elements to inhibit the oligomerization.[3] The most well known and widely used current routes to the representative inorganic polymers, polysiloxisanes,[4] polyphosphazenes,[5] and poly(carbosilane)s[6] involve a ring-opening polymerization (ROP) reaction, which is induced by heat, anionic or cationic initiators, or metal catalysts. With this in mind, the polymerization behavior of other inorganic rings, such as polysilanes,[7] carbophosphazenes[8] and thiophosphazenes,[9] has recently attracted much attention. Though the use of inorganic rings for ring-opening homopolymerization has been successfully developed, only a few examples of the copolymerization of inorganic homocycles with organic comonomers have been reported.[10] Cyclooligophosphines are monocyclic compounds with rings built exclusively of phosphorus atoms, which are interesting owing to their ability to form complexes with metal carbonyls and transition metal salts.[11] However, there are few reports on reactions of cyclooligophosphines with organic compounds.[11a,12] It was reported that the triple bond of phenylacetylene (PA) reacts with a phosphorus-phosphorus bond of a diphosphine compound (R_2P-PR_2, R = Me or Ph) in the presence of a catalytic amount of 2,2'-azobisisobutyronitrile (AIBN) to produce the inserted compound (R_2P-CPh=CH-PR_2).[13] It can be speculated, therefore, that a polymer containing phosphorus atoms in the main chain would be obtained by the insertion of PA into P-P bonds of cyclic phosphorus compounds instead of diphosphines. Phosphorus containing polymers have found a variety of important uses including flame retardants,[14] ionic conducting materials,[15] and easily separable supports for metal catalysts.[16] Recently, conjugated organophosphorus polymers were

synthesized and showed interesting features such as significant extension of conjugation along the polymer backbone via the lone pair on P, fluorescent properties, and electron-donating character.[17] However, examples of the conjugated organophosphorus polymers are still rare, and thus to construct a novel structure of them is interesting. This chapter 7 describes ring-collapsed radical alternating copolymerization (*RCRAC*) of cyclooligophosphine with PA which produced a novel organophosphorus polymer, poly(vinylene-phosphine).

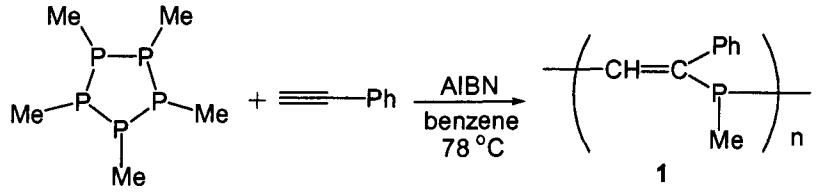
Results and Discussion

Synthesis and Characterization of Poly(vinylene-phosphine). The methyl-substituted cyclooligophosphine was synthesized by the reduction of methyldichlorophosphine with lithium according to the literature procedure (Scheme 1).[18] It is known that the five-membered ring structure, pentamethylcyclopentaphosphine, *cyclo*-$(MP)_5$, is mainly formed by this method and exclusively obtained by distillation under reduced pressure. Under a nitrogen atmosphere, the phosphorus ring compound reacted with PA in the presence of a catalytic amount of AIBN at 78 °C in oxygen-free benzene to produce the copolymer with the structure of 1 : 1 alternating methylphosphine (MP) and vinylbenzene units (Scheme 2). The obtained poly(vinylene-phosphine) **1** was purified by reprecipitation from benzene to *n*-hexane and then freeze-dried to give a light yellow powder in 46 % yield. The relatively low yield was attributable to the removal of low molecular weight materials by the reprecipitation. The resulting polymer was soluble in common organic solvents such as chloroform, THF, benzene, and toluene.

Scheme 1



Scheme 2



Gel permeation chromatography (GPC) analysis (chloroform) of the obtained polymer **1** showed a single peak and resulted in an estimated number-average molecular weight (M_n) of 2500 (vs polystyrene standards) with a polydispersity index (PDI; M_w/M_n) of 1.25. The degree of polymerization (DP) was 16. The structure of **1** was supported by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopies. The ^{1}H NMR spectrum (Figure 1) showed peaks in aromatic (6.6 – 7.6 ppm) and vinyl regions (5.89 ppm) and a peak assignable to the methyl proton at 0.80 ppm. The chemical shift of the vinyl proton suggested that a trans-isomer was predominantly obtained.[13] Small peaks around 1.2 – 1.6 ppm can be attributed to the terminal methyl proton from AIBN. The integral ratio of the peaks of the phosphorus-methyl proton, the end group (from AIBN), and the vinyl proton was $3.0_0 : 0.6_6 :$ 1, indicating the polymer main chain structure of the 1 : 1 alternating unit of MP and PA with a DP of 17. This ratio also suggests that the polymer end structure is the isobutyronitrile group from AIBN (Chart 1, calculated ratio; 3.17 : 0.70 :1). This result of end-group analysis is in agreement with the GPC analysis. In contrast to the poly(vinylene-arsine) synthesized by the radical reaction of cyclooligoarsines with PA using AIBN, of which ^{1}H and

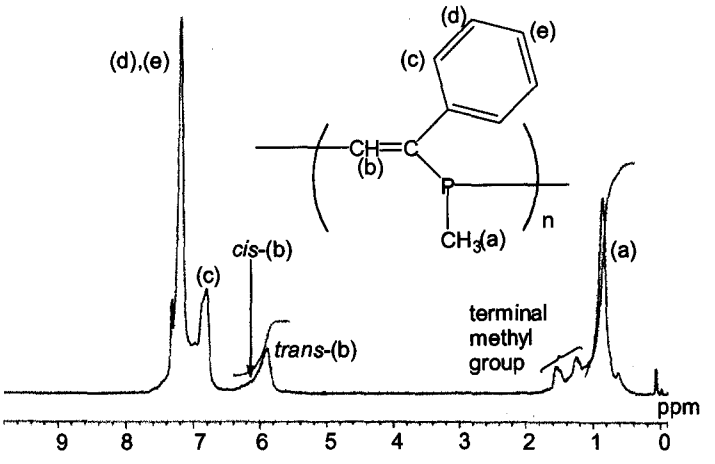
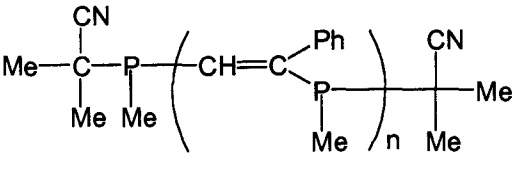


Figure 1. ^{1}H NMR spectrum of **1**.

Chart 1



^{13}C NMR spectra showed no obvious peaks attributable to end groups,[19] poly(vinylene-phosphine) **1** possesses well-defined terminal structure. This result suggests that the P radical with the isobutyronitrile group acted as an end-capping agent during the copolymerization, while the copolymerization system of cyclooligoarsine with PA had few end-capper. This fact might also contribute the lower molecular weight of **1** than that of methyl-substituted poly(vinylene-arsine) **2** synthesized by the same methodology (M_n = 11500, yield 46 %) in Chapter 1. The ^{13}C NMR spectrum (Figure 2) showed only one sharp resonance for the methyl carbon at 11.9 ppm and the ^{31}P NMR (Figure 3) spectrum exhibited one peak at – 28.4 ppm. These results were compatible with the fact that the polymer backbone possessed no oxidized phosphorus atom and no phosphorus-phosphorus bond.

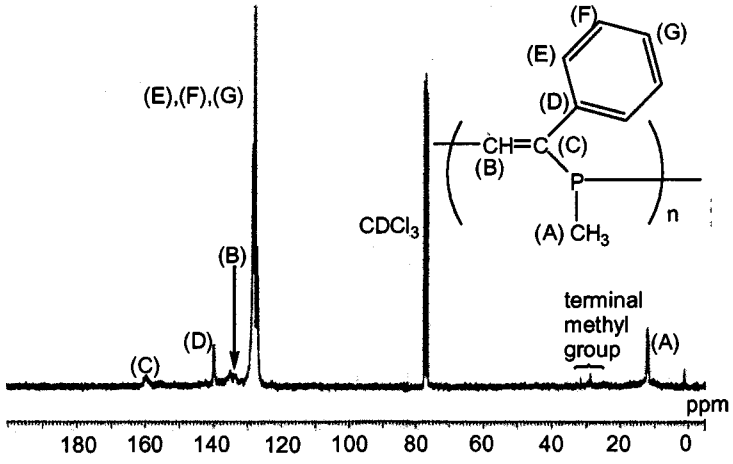


Figure 2. ^{13}C NMR spectrum of **1**.

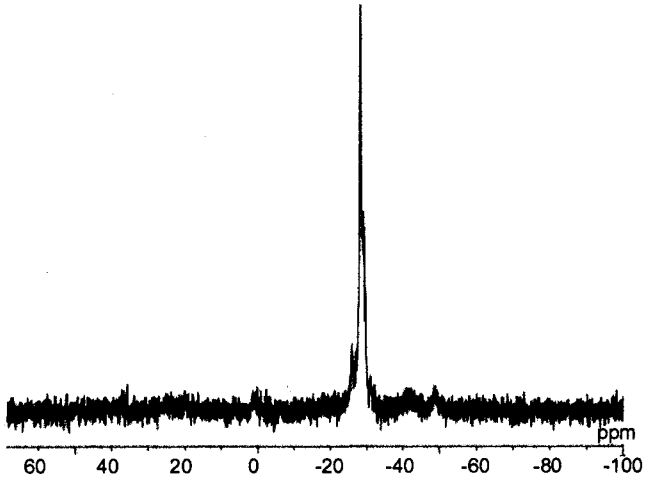


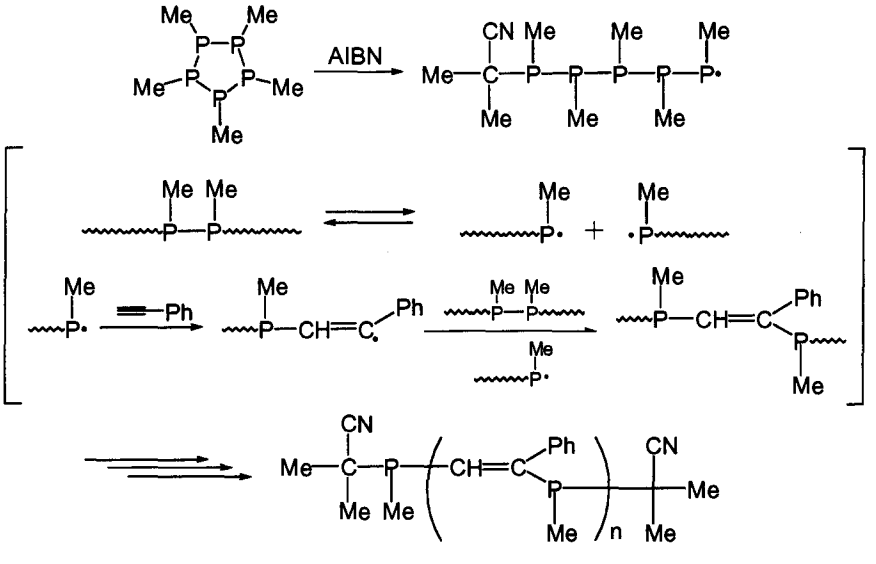
Figure 3. ^{31}P NMR spectrum of **1**.

The poly(vinylene-phosphine) **1** is reasonably air- and moisture-stable in the solid state; no change was observed in the GPC trace and ^{31}P NMR spectrum after **1** in the solid state was exposed to air for several days. The polymer **1** was reacted with elemental sulfur in dichloromethane to yield phosphine sulfide of which ^{31}P NMR spectrum showed a peak at 39.8 ppm and no peak around –28 ppm. The GPC trace exhibited no significant change compared to that before sulfuration.

The phenyl-substituted cyclooligophosphine, *cyclo*-$(PP)_5$, which had poor solubility in benzene, was also treated with PA in the presence of AIBN in refluxing benzene. The reaction mixture became homogeneous within about 30 min, suggesting the collapse of the ring structure of *cyclo*-$(PP)_5$. No polymer, however, was obtained after stirring the mixture for 8 h. Phenyl-substituted phosphorus radical was not reactive enough to add to the carbon–carbon triple bond of PA.

Mechanism of the Copolymerization. The copolymerization of *cyclo*-$(MP)_5$ with PA should have proceeded in a similar way to that of cyclooligoarsine with PA as described in Chapter 1 (Scheme 3). First, AIBN cleaved the P-P bond of *cyclo*-$(MP)_5$ to produce an open-chain phosphorus oligomer with phosphorus radical. The P-P bonds of the open-chain oligomer caused spontaneous homolytic cleavage. The produced P radical attacked the ethynyl group of PA to produce a vinyl radical, which reacted immediately with the P radical or P-P bond to result in the formation of a new C-P bond. During the

Scheme 3



copolymerization the P radical with the isobutyronitrile group acted as an end-capping agent. Since the vinyl radicals were less stable than the P radicals, the copolymerization proceeded highly alternatingly. The obtained copolymer **1** had no P-P bonds in the main chain since the cleavage of phosphorus-phosphorus bonds completed much faster than formation of the vinyl radicals. Polymer **1** had no C=C-C=C moieties in the backbone because the vinyl radical rarely added to the triple bond of PA to form a vinyl radical. In addition, homo-coupling of the vinyl radical was ignored due to its low concentration.

Optical Properties of Poly(vinylene-phosphine). The electronic structure of polymer **1** was investigated by using UV-vis spectroscopy. Figure 4 shows an absorption spectrum of **1** recorded in chloroform at room temperature. Not only strong absorption in the UV region derived from π–π^* transition of benzene ring, but also small absorption in the visible region was observed. The absorption edge located at around 500 nm. It is assumed that n–π^* transition in the main chain brought about the lower energy absorption[20] as seen in the case of poly(phenylene-phosphine)s.[21]

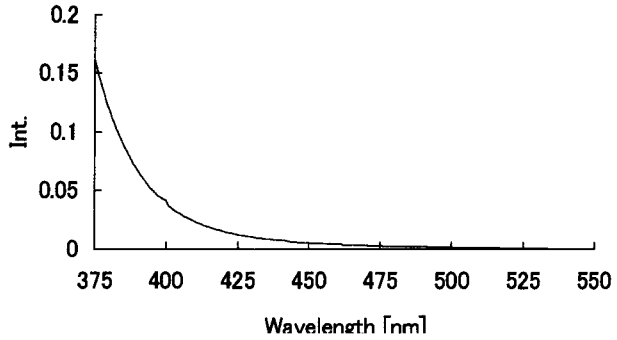


Figure 4. UV-vis absorption spectrum of **1** in $CHCl_3$ measured at room temperature.

Polymer **1** showed fluorescent properties. The fluorescence and excitation spectra of a dilute chloroform solution of **1** measured at room temperature are shown in Figure 5a. The emission was observed in the visible blue-green region with a peak at 470 nm and a shoulder peak at 500 nm by irradiation at 430 nm. In the excitation spectrum of **1** monitored at 470 nm, the absorption peak was not observed in the UV region but in the visible region with two peaks at 400 nm and 430 nm. This means that the absorption of **1** in the UV region and the absorption in the visible region are originated from different absorbing species. The

emission of **1** results from only the absorption of the n–π* transition. When the dilute chloroform solution was irradiated at 400 nm, the same spectrum as in Figure 5a was observed.

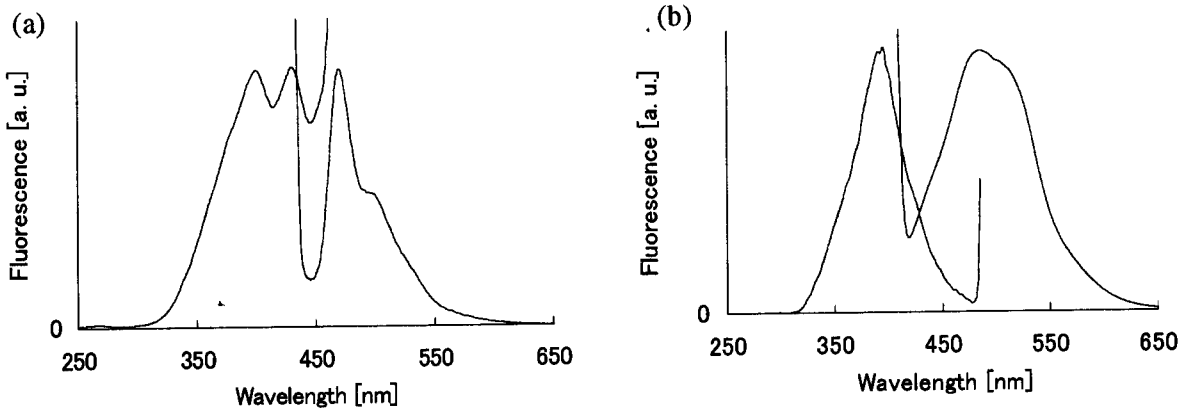
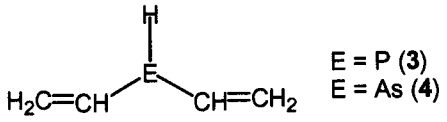


Figure 5. (a) Emission (right) (excited at 430 nm) and excitation (left line) (emitted at 470 nm) spectra of **1**. (b) Emission (right line) (excited at 400 nm) and excitation (left line) (emitted at 485 nm) spectra of **2**. All measurements were carried out in chloroform at room temperature.

The methyl-substituted poly(vinylene-arsine) (**2**), arsenic-analogue to **1**, also exhibited a blue-green emission by excitation with ultraviolet light (Figure 5b). The excitation spectrum of **2** showed a peak at 396 nm. It is assumed that the bathochromic shift observed in excitation spectrum of **1** compared with that of **2** is attributed to the conformation of phosphorus or arsenic atom in the main chain. A calculation using the PM3 Hamiltonian suggested that the bond angle C-E-C in divinylphosphine **3** is larger than that in an arsenic-analogue **4** (Chart 2).[22] This leads to the assumption that **1** should take more linear conformation than **2**, inducing a more effective delocalization along the main chain. Furthermore, the inversion barrier at phosphorus atom in the backbone of **1** should be smaller than that at arsenic atom in the backbone of **2**.[23] This flexibility of **1** must increase the conformational planarity in the main chain more effectively than that of **2**.

Chart 2



Summary

This chapter describes the preparation of a novel conjugated polymer containing phosphorus atom in the main chain by ring-collapsed radical alternating copolymerization (*RCRAC*) of cyclooligophosphine with phenylacetylene. The investigations suggest the emission properties of the polymer attributable to the n–π* transition in the main chain. The present work demonstrates the utility and generality of the radical copolymerization method for the synthesis of heteroatom-including polymers.

Experimental Section

Materials. Unless otherwise noted, all reagents and chemicals were purchased from Wako Pure Chemical Industries, Ltd. Benzene was dried over CaH_2, distilled, bubbled with a stream of nitrogen before use. *n*-Hexane (water < 30 ppm) was used without further purification. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Phenylacetylene (PA) was purchased from Aldrich and purified by distillation under reduced pressure. Pentamethylcyclopentaphosphine, *cyclo*-$(MP)_5$, and pentaphenylcyclopentaphosphine, *cyclo*-$(PP)_5$, were synthesized using literature procedures.[18]

Equipment. All reactions and manipulations were carried out under an atmosphere of prepurified nitrogen using Schlenk techniques. ^1H, ^{13}C, and ^{31}P NMR spectra were obtained using a JEOL JNM-EX270 instrument for solutions in $CDCl_3$ and were referenced to $SiMe_4$ (TMS) or H_3PO_4. Gel permeation chromatography (GPC) was carried out on a TOSOH UV-8011 and RI-8000 (Shodex K-803L column) using $CHCl_3$ as an eluent after calibration with standard polystyrene.

Polymerization. Under a nitrogen atmosphere, a benzene solution of 2,2'-azobisisobutyronitrile (AIBN) (30 mg, 0.18 mmol) was added to a refluxing solution of *cyclo*-$(MP)_5$ (0.529 g, 2.29 mmol) and phenylacetylene (PA) (1.17 g, 11.5 mmol) in benzene (4.0 mL). After stirring for 8 h, the reaction mixture was poured into *n*-hexane to precipitate a polymeric material. The resulting polymer was purified by reprecipitation into *n*-hexane three times and freeze-dried for 10 h to yield the corresponding poly(vinylene-phosphine) **1** as a bright yellow powder (0.78 g, 46 % yield). ^1H-NMR (δ,

ppm): 0.80 (P-CH_3), 5.83 (C=CH), 6.75 (ArH_o), 7.12 (ArH_m, ArH_p). ^{13}C-NMR (δ, ppm): 11.9 (As-CH_3), 126-130 ($C_{Ar}H_o$, $C_{Ar}H_m$, $C_{Ar}H_p$), 133-136 (C=*C*H), 139.8 (C_{Ar}-C), 159.5(*C*=CH). ^{31}P-NMR (δ, ppm): -28.5.

Sulfuration of 1. A solution of **1** (0.30 g, 2.0 mmol) in dichloromethane (20 mL) was added to a suspension of S_8 (0.15 g, 0.58 mmol) in dichloromethane (10 mL). The suspension was stirred for 48 h and then the excess sulfur was removed by filtration. The solvent was distilled away and the obtained polymer was analyzed by ^{31}P NMR spectroscopy. ^{31}P-NMR (δ, ppm): 39.8.

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Chapter 8

Radical Copolymerization of Cyclic Diarsine with Vinyl Monomers

Abstract: 1,2,4,5-Tetramethyltetrahydrodiarsenine (**1**), a cyclic diarsine compound, was stirred with styrene and a catalytic amount of 2,2'-azobis(isobutyronitrile) (AIBN) as a radical initiator at 80 °C for 8 h in toluene to give a copolymer containing arsenic atoms in the backbone. The gel permeation chromatography (GPC) trace of the copolymer showed a single peak. The number-average molecular weight of the copolymer was estimated to be more than ten thousands by GPC analysis ($CHCl_3$, polystyrene standards). The structure of the copolymer was confirmed by ^1H NMR and ^{13}C NMR spectra. According to the integral ratio of peaks in the ^1H-NMR spectrum, the content of **1** unit in the copolymer was smaller compared to the monomer feed ratio of **1**. Radical copolymerization of **1** with methyl methacrylate (MMA) also provided the corresponding copolymer in the presence of AIBN, while copolymerization with vinyl acetate (VA) yielded no polymeric material.

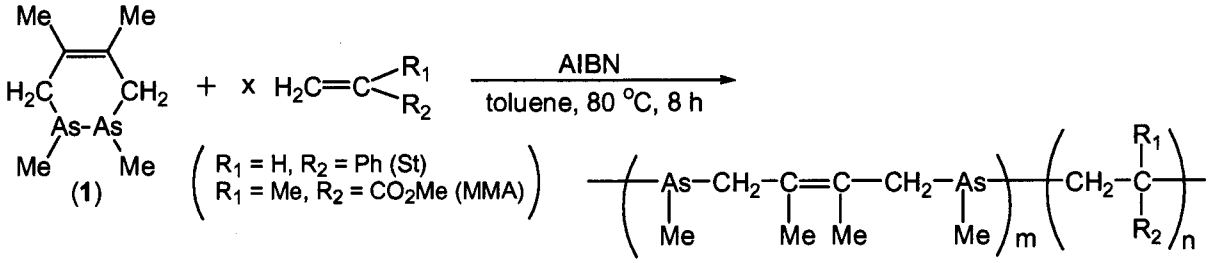
Introduction

Cacodyl (tetramethyldiarsine, $Me_2AsAsMe_2$) is the first synthetic organometallic compound[1] and played a vital role in the development of organometallic chemistry at the early stage.[2] Thereafter, a wide variety of diarsine compounds have been prepared.[3] Formation of cacodyl and other symmetric or asymmetric diarsines has been achieved in various ways, including reduction of $R_2As(O)OH$ by hypophosphorus acid,[4] oxidation of R_2AsH with Cl_2, NH_2Cl, or Me_2NCl,[5] reaction of R_2AsCl with R'_2AsH,[6] and so on. The considerable reactivity of R_2AsAsR_2 is illustrated by reactions with moist air,[7] diorganodichalcogenides (R'EER', E = S, Se, Te),[8] alkali metals,[9] and carbon-carbon triple bonds.[10] All reactions lead to cleavage of the arsenic-arsenic bond. In recent years, there have been some interests in the applications of diarsine compounds as ligands in transition metal complexes.[11] Among organic diarsine compounds, there have been a few examples of cyclic organodiarsines.[12] Their reactions with alkali metals[13] or complexation with transition metals[12b] were also reported.

Cyclic disulfides copolymerize with vinyl monomers by homolytic reactions. For example, styrene copolymerizes with 1-oxa-3,4-dithiacycloheptane (a seven-membered cyclic disulfide)[14] or lipoamide (a five-membered cyclic disulfide with an amide group)[15] by chain transfer of propagating styryl radicals to the cyclic disulfides to give copolymers with sulfide linkages in the main chain. By ultraviolet irradiation, the disulfide linkage of trimethylene disulfide (a five-membered cyclic disulfide) is cleaved to form thiyl radicals and copolymerized with styrene.[16] Therefore, cyclic compounds with element-element bonds which cause homolysis are attractive as comonomers in radical copolymerization of vinyl monomers. On the other hand, chapter 1 describes the synthesis of organoarsenic polymers, poly(vinylene-arsine)s,[17] by ring-collapsed radical alternating copolymerization (*RCRAC*) of organoarsenic homocycles whose rings were built exclusively of arsenic atoms,[18] with phenylacetylene. The poly(vinylene-arsine)s were the first organic polymers bearing arsenic atoms in the main chains. The homolytic cleavage of the arsenic-arsenic bonds of organoarsenic homocycles proceeded completely during the copolymerization to yield the copolymers which had no As-As bond in the backbones.

In contrast to the well-studied radical copolymerization of the cyclic disulfides with vinyl monomers, to our knowledge, no attempts have been made to investigate the reactivity of cyclic diarsine compounds in radical polymerization. Since the arsenic-arsenic bond of diarsines is cleaved easier than the arsenic-carbon bond,[3] the cyclic diarsines may copolymerize with other organic compounds by the cleavage of the diarsenic linkage in the presence of a radical initiator similarly to the organoarsenic homocycles. In the present chapter, 1,2,4,5-tetramethyltetrahydrodiarsenine (**1**), a six-membered diarsine compound, was employed as a comonomer in radical copolymerization of vinyl monomers, i. e., styrene (St) and methyl methacrylate (MMA) (Scheme 1).

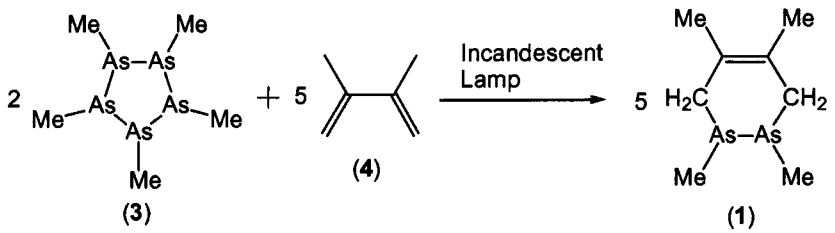
Scheme 1



Results and Discussion

Copolymerization of 1 with Styrene. 1,2,4,5-Tetramethyltetrahydrodiarsenine (**1**) was synthesized by photoreaction between pentamethylcyclopentaarsine (**3**) and 2,3-dimethyl-1,3-butadiene (**4**) being irradiated with an incandescent lamp (Scheme 2).[12a] Though the detailed mechanism of the reaction is unclear, **1** might be formed via radical species of arsenic and butadiene.[12a] While **3** copolymerized with phenylacetylene in the presence of AIBN at 80 °C,[17] a treatment of **3** with **4** and a catalytic amount of AIBN at 80 °C in toluene caused no reaction. The cyclic diarsine **1** is a colorless liquid with a little

Scheme 2



repugnant odor and has a good miscibility in common organic solvents such as toluene, benzene, tetrahydrofuran, and chloroform.

Copolymerization of **1** with St was carried out at 80 °C for 8 h under a nitrogen atmosphere (Scheme 1, R_1 = H, R_2 = Ph). A catalytic amount of 2,2'-azobisisobutyronitrile (AIBN) (1.8 mol % of **1**) was used as a radical initiator. The feed ratio of **1** was 25 % of the total monomers. A white powdery polymer (**2**) was obtained by reprecipitation from toluene to methanol (yield; 13 %). The GPC (using chloroform as an eluent) trace of **2** showed a single peak, and the number-average molecular weight of **2** was estimated to be 12 000 (Table 1, Run 1). The molecular weight distribution of the copolymer obtained was relatively narrow (M_w/M_n = 1.2) due to the removal of low molecular weight materials by the reprecipitation.

Table 1. Results of Copolymerization of **1** with Styrene[a]

Run	St / **1**[b]	[AIBN] /[**1**]$_0$	Yield, %[c]	m : n[d]	M_n[e]	M_w / M_n[e]
1	3.0	0.018	13	1 : 8.0	12 000	1.2
2	3.0	0	0			
3	0	0.018	0			
4	1.0	0.030	trace			
5	2.0	0.018	8	1 : 6.0	12 600	1.2
6	4.5	0.018	20	1 : 12.0	16 400	1.2
7	6.0	0.018	16	1 : 16.0	16 300	1.2

[a] In toluene; reaction temperature, 80 °C; reaction time; 8 h. [b] Molar ratio of styrene to **1**. [c] Isolated yield after reprecipitation from toluene to methanol. [d] Estimated by ^{1}H NMR. [e] Estimated by GPC analysis in chloroform on the basis of polystyrene calibration.

By characterization of **2** with ^{1}H NMR and ^{13}C NMR spectra, **1** was found to give a copolymer with St, which had arsenic linkages in the main chain. The ^{1}H NMR spectrum of **2** (Figure 1a) exhibited resonances for the aromatic (6.2-7.6 ppm) and aliphatic (0.8-2.8 ppm) protons. Those peaks were broad in comparison with the peaks in the spectrum of polystyrene (Figure 1b) which was prepared under the same condition as that of the synthesis of **2** without **1**.

The integral ratio of the peaks of the aromatic protons to those of the aliphatic protons in Figure 1a revealed the copolymer composition of **2**, m : n = 1 : 8.0. The content of **1** unit in the copolymer was smaller than the monomer feed ratio of **1**. The ^{13}C NMR spectrum of **2** (Figure 2a) showed several peaks due to **1** unit in the copolymer other than the peaks for styrene unit (Figure 2b). The assignments of the peaks are listed in Figure 2a, which were supported by a DEPT spectrum.

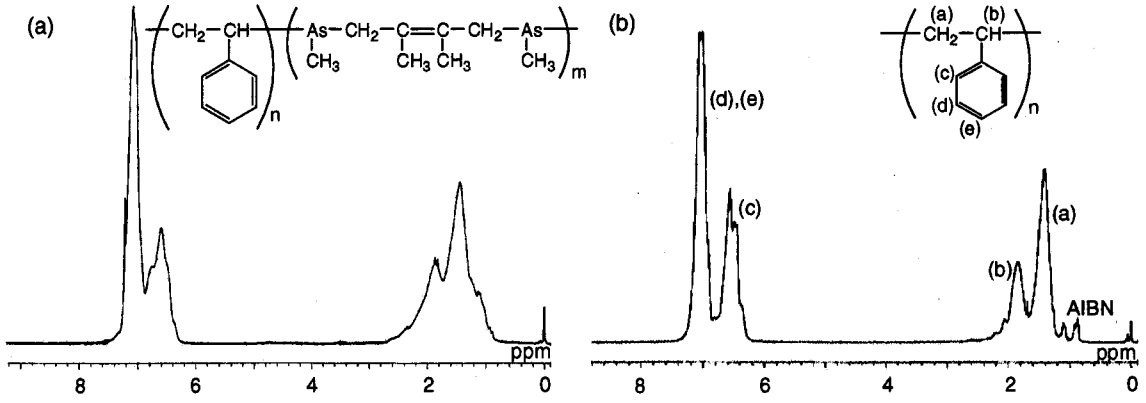


Figure 1. ^{1}H NMR spectra of **2** (a) and polystyrene (b) recorded in $CDCl_3$.

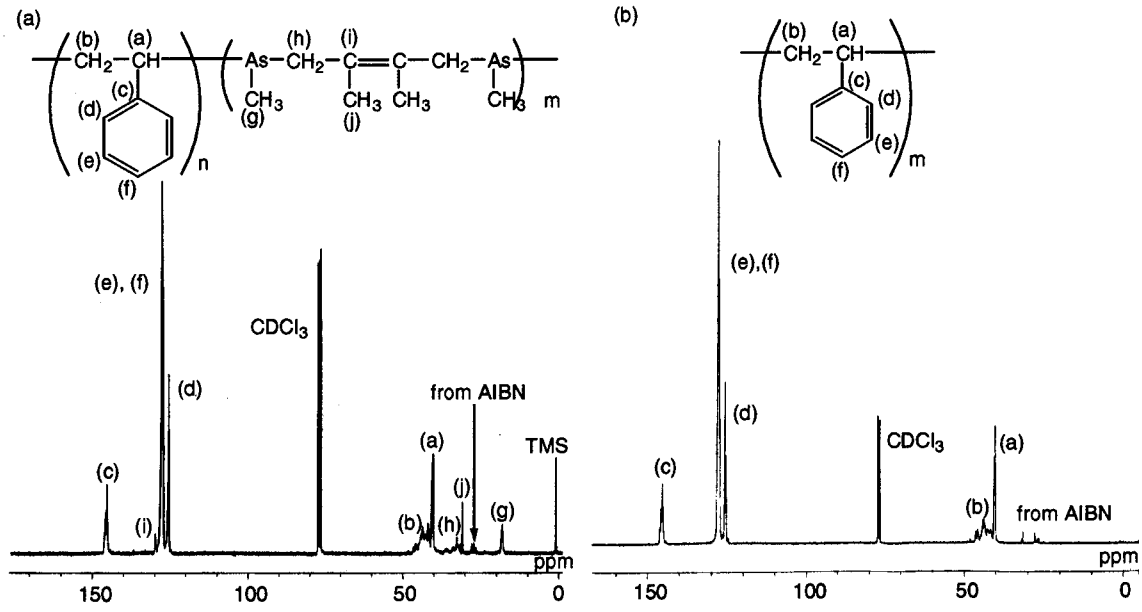


Figure 2. ^{13}C NMR spectra of **2** (a) and polystyrene (b) recorded in $CDCl_3$.

The copolymerization of **1** with St in the absence of AIBN resulted in no high-molecular-weight material (Table 1, Run 2), suggesting that the radical copolymerization was initiated by the attack of the radicals from AIBN to **1** or St. During the copolymerization, the propagating arsenic radicals might react with the diarsine linkage of **1** to form the arsenic-arsenic bonds in the copolymer main chain. The copolymer obtained, however, possessed no As-As bonds in the main chain, which was proved by the ^{13}C NMR spectrum of **2** (Figure 2b) exhibiting a single, sharp peak assigned to As*C*H$_3$. The diarsine linkage in the backbone could be easily cleaved spontaneously or by the attack of propagating styryl radical.[7,17] This also explains the fact that no polymer was formed in the reaction of **1** with a catalytic amount of AIBN (Table 1, Run 3).

The radical copolymerization of **1** with St in various feed ratios was carried out (Table 1, Run 1 and 4-7). The copolymerization of **1** with an equimolar amount of St (Run 4) yielded a small quantity of the copolymer which was not separated completely from low-molecular-weight materials by reprecipitation from toluene to methanol. Due to the comparable amount of **1**, which has low homopolymerizability, to that of St, the polymeric material in small quantity was obtained. When twice or more amount of St compared to that of **1** was employed (Run 1 and 5-7), the copolymer was isolated by reprecipitation. The copolymer compositions were estimated from the integral ratio in ^1H NMR spectra and are listed in Table 1. The content (mol %) of **1** unit in the copolymer was almost proportional to the monomer feed ratio (mol %) of **1** in Run 1 and 5-7, and the proportionality constant was 0.42–0.44.

Reactions of Cyclic Diarsine (1) and Arsenic Homocycle (3) with Organic Compounds Having Carbon-carbon Multiple Bonds. Cyclic diarsine (**1**) was gradually cleaved to form pentamethylcyclopentaarsine (**3**) and 2,3-dimethyl-1,3-butadiene (**4**) at room temperature. To exclude the possibility of this process involved in the copolymerization, we attempted the following experiments. Treatment of St with **3** and **4** using a catalytic amount of AIBN in toluene at 60 °C[19] for 8 h produced no polymeric material but the starting monomers. A toluene solution of St and **4** was stirred at 60 °C in the presence of a catalytic amount of AIBN. No polymeric material was obtained. It is known that radical polymerization of butadienyl compounds in a homogeneous (solution or bulk) system yields

only low-molecular-weight polymer.[20] Butadienyl radical is so stable and long-lived that the recombination reaction takes place frequently. These facts indicate that the existence of **4** in the reaction mixture prevented the progress of the terpolymerization of St, **3** and **4** and the copolymerization of St and **4**. The radical copolymerization of **1** with St proceeded due to the absence of the butadienyl radical. A mixture of St, **3**, and **4** without solvent was stirred while being irradiated with an incandescent lamp for 10 h. Although **1** was formed, no polymer was obtained. Radical species of arsenic and butadiene, which were formed by the irradiation of the incandescent lamp, showed no reactivity toward St.

Stirring a mixture of St, **3**, and a catalytic amount of AIBN in toluene at 80 °C produced a purple-black precipitate which was insoluble in any solvents and fuming in the air. Stirring a mixture of St and **3** being irradiated with an incandescent lamp resulted in the formation of the same purple-black precipitate. No polystyrene or copolymer containing styrene unit was obtained in both cases. The troublesome precipitate must have been linear polymethylarsines which stacked with each other to form a ladder structure.[21] Though it remains to be seen whether radicals from AIBN reacted with styrene or the organoarsenic homocycle, **3** inhibited the radical polymerization of styrene. The copolymerization of **1** with phenylacetylene was attempted using AIBN as a radical initiator but resulted in no polymeric materials, while **3** showed an excellent copolymerizability with acetylenic compounds.[17] The photoreaction of **1** with phenylacetylene by an incandescent lamp also led to no polymer. In brief, cyclooligoarsine **3** did not copolymerize with styrene but with phenylacetylene; cyclic diarsine **1** did not copolymerize with phenylacetylene but with styrene. The reactivity of the arsenic radical that arose from the homolytic cleavage of the arsenic-arsenic bond of **1** was different from that of the As radical from **3**.

Copolymerization of 1 with Other Vinyl Monomers. The radical copolymerization of **1** was carried out with methyl methacrylate (MMA) instead of styrene with a feed ratio, **1** : MMA = 1 : 3 (Scheme 1, R_1 = Me, R_2 = CO_2Me). After reprecipitation into methanol, the polymeric material was obtained (yield = 13 %). The GPC trace of the polymer obtained showed a single peak. The number-average molecular weight (M_n) and the molecular weight distribution (M_w/M_n) of the polymer were M_n = 20 500 and M_w/M_n =1.4, respectively by the GPC measurement. By characterization with ^1H and ^{13}C NMR spectra, the polymeric

material was the copolymer of **1** and MMA, and the copolymer composition was estimated to be **1** : MMA = 1 : 6.4. The content of **1** unit in the copolymer obtained was higher than that of **1** unit in copolymer **2**. This fact indicates that the electron-accepting nature of MMA brought about the more frequent attack of MMA radical to the As-As bond of **1** which is electron rich due to the lone pairs on arsenic atoms.

The copolymerization of **1** with vinyl acetate (VA) with a catalytic amount of AIBN was also attempted but yielded no polymeric material. It can be presumed that, in this system, all of the radicals from AIBN reacted with **1** and the produced arsenic radicals could not attack VA due to the lack of conjugative substitution to the vinyl group.

Summary

In summary, the six-membered cyclic diarsine compound, 1,2,4,5-tetramethyltetrahydro-diarsenine (**1**), was copolymerized with St and MMA to give the polymer containing arsenic atoms in the main chain in the presence of radical initiator. The polarity and the conjugative stabilization of the substitution of the vinyl group affected the content of the vinyl monomer unit in the copolymer. This radical copolymerization proceeded under mild conditions and is, therefore, useful for the synthesis of novel polymers with arsenic linkages in the backbone and various functional groups as pendants.

Experimental Section

Materials and Instruments. Unless otherwise noted, all reagents and chemicals were purchased from Wako Pure Chemical Industries, Ltd. Toluene was dried over CaH_2, distilled, and bubbled with a stream of nitrogen before use. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Vinyl monomers were purified by the usual method. 2,3-Dimethyl-1,3-butadiene (**4**), and phenylacetylene were purchased from Aldrich and purified by distillation under reduced pressure. Pentamethylcyclopentaarsine (**3**) was synthesized using a literature procedure.[22] ^{1}H-NMR spectra were recorded on a 270 MHz JEOL-JNM-GX270 NMR spectrometer. ^{13}C-NMR spectra were recorded on a 67.5 MHz JEOL-JNM-GX270 NMR spectrometer. Gel permeation chromatographic analysis was carried out on a Shodex K-803 by using $CHCl_3$ as an eluent after calibration with

polystyrene standards.

Synthesis of 1,2,4,5-Tetramethyltetrahydrodiarsenine (1). Cyclic diarsine **1** was prepared according to ref 12a as follows. Under a nitrogen atmosphere, a mixture of **3** (2.92 g, 6.48 mmol) and **4** (2.92 g, 35.5mmol) was irradiated by an incandescent lamp (100W) and stirred overnight. The bulk mixture changed its color from yellow to colorless. Fractional distillation of the mixture provided pure 1,2,4,5-tetramethyltetrahydrodiarsenine (**1**) as colorless oil; yield 2.6 g (61 %); b.p. 57 °C / 4.4 mmHg. ^{1}H NMR (δ, ppm): 0.96 (s, 6H, C-C*H*$_3$), 1.82 (s, 6H, As-C*H*$_3$), 2.15 (d, 2H, C*H*$_2$), 2.36 (d, 2H, C*H*$_2$), (lit. δ 0.90 (6H), 1.80 (6H), 2.09 (2H), 2.40 (2H)); ^{13}C NMR (δ, ppm): 4.6 (As-*C*H$_3$), 21.2 (*C*H$_2$), 29.3 (C-*C*H$_3$), 127.3 (-*C*(Me)=*C*(Me)-).

Polymerization. Copolymerization of 1 with Styrene (St). A typical radical copolymerization procedure was conducted as follows. Under a nitrogen atmosphere, a mixture of **1** (0.436 g, 1.66 mmol), St (0.520 g, 4.99 mmol), and a catalytic amount of 2,2'-azobisisobutyronitrile (AIBN) (5.0 mg, 0.03 mmol) in toluene (2.0 ml) was stirred at 80 °C for 8 h. A high-molecular-weight material obtained was precipitated with methanol and separated by centrifugation. After reprecipitation from toluene to methanol, the product was freeze-dried for 10 h. A white powdery copolymer (**2**) was obtained (0.121 g, 13 %). ^{1}H NMR (δ, ppm): 6.2–7.6 (Ar-*H*), 0.8-2.8 (aliphatic *H*). ^{13}C NMR (δ, ppm): 146 (C_{Ar}-C), 130 (*C*=*C*), 127-129 ($C_{Ar}H_m$, $C_{Ar}H_p$), 126 ($C_{Ar}H_o$), 41.8-44.1 (*C*H$_2$-CH), 40.4 (CH$_2$-*C*H), 31.5-34.0 (As-*C*H$_2$), 30.8 (C-*C*H$_3$), 26.5-27.9 (*C*H$_3$ from AIBN), 18.2 (As-*C*H$_3$).

Copolymerization of 1 with Methyl Methacrylate (MMA). **1** (0.447 g, 1.71 mmol), MMA (0.513 g, 5.12 mmol), AIBN (5.0 mg, 0.03 mmol), and toluene (2.0 ml) were employed. The corresponding copolymer was obtained (0.123 g, 13 %). ^{1}H NMR (δ, ppm): 3.5–3.8 (OC*H*$_3$), 0.7-2.4 (other aliphatic *H*).

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List of Publications

Chapter 1

Synthesis of Poly(vinylene-arsine)s: Alternating Radical Copolymerization of Arsenic Atomic Biradical Equivalent and Phenylacetylene

Naka, K.; Umeyama, T.; Chujo, Y. *J. Am. Chem. Soc.* **2002**, *124*, 6600-6603.

Chapter 2

Spontaneous Ring-Collapsed Alternating Copolymerization of Homocyclic Arsenic Compound and Phenylacetylene

Umeyama, T.; Naka, K.; Chujo, Y. submitted to *J. Am. Chem. Soc.*

Chapter 3

Radical Copolymerization of Acetylenic Compounds with Phenyl-Substituted Cyclooligoarsine: Substituent Effect and Optical Properties

Umeyama, T.; Naka, K.; Nakahashi, A.; Chujo, Y. *Macromolecules* in press.

Chapter 4

Ring-Collapsed Radical Alternating Copolymerization (*RCRAC*) of Organoarsenic Homocycle with Aliphatic Acetylenes

Umeyama, T.; Naka, K.; Chujo, Y. submitted to *J. Polym. Sci. Part A: Polym. Chem.*

Chapter 5

Radical Terpolymerization of Organoarsenic Homocycle, Phenylacetylene, and Vinyl or Butadienyl Monomers

Umeyama, T.; Naka, K.; Chujo, Y. submitted to *Macromolecules.*

Chapter 6

Synthesis and Properties of Cross-Linked Poly(vinylene-arsine)

Umeyama, T.; Naka, K.; Bravo, M. D.; Nakahashi, A.; Chujo, Y. submitted to *Polym. Bull.*

Chapter 7

Synthesis of Poly(vinylene-phosphine)s: Ring-Collapsed Radical Alternating Copolymerization (*RCRAC*) of Cyclooligophosphine with Phenylacetylene

Umeyama, T.; Naka, K.; Chujo, Y. to be submitted.

Chapter 8

Radical Copolymerization of Cyclic Diarsine with Vinyl Monomers

Umeyama, T.; Naka, K.; Chujo, Y. *J. Polym. Sci. Part A: Polym. Chem.* in press.

Other Publications

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